

MASS SPECTROMETRIC STUDY OF THE PRODUCTS
OBTAINED FROM FAST CRYOGENIC QUENCHING
OF SEVERAL REACTIONS INVOLVING ATOMIC
HYDROGEN OR ATOMIC OXYGEN

A THESIS

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SUMMARY

The reactions of hydrogen and oxygen atoms with several simple compounds followed by rapid quenching to cryogenic temperatures have been studied with the use of a unique low temperature inlet system to a mass spectrometer. The rapid quenching was carried out in an attempt to stabilize the initial reaction products, and the inlet system permitted the detection of any compounds which might be stable only at low temperatures. The systems that were studied were the reactions of oxygen atoms with ammonia, acetylene, ethylene, and ethane; and the reaction of hydrogen atoms with nitric oxide.

The atoms were produced by means of an efficient radio frequency electrodeless electric discharge arrangement which consisted of a 50-turn copper coil and an impedance matching network. The network insured the maximum power transfer from the transmitter to the plasma and hence, maximum production of atomic species.

The resulting mixture of atomic and molecular species contacted a second gaseous reactant in a pyrex reactor cooled to very low temperatures, thereby resulting in fast quenching of the reaction products. The quenching temperature was varied from 77° to 100°K and the reactions occurred in a pressure range of 0.5 to 2.5 mm Hg. The low temperatures were produced by immersing the reactor in a dewar of a suitable liquid refrigerant.

The reaction products were studied during a controlled warm-up from the quenching temperature by use of the low temperature inlet system

to the mass spectrometer. The inlet system was simply a passageway from the reactor to the ion source that was maintained at essentially the same temperature as that of the reactor. This was accomplished by immersing both the inlet system and the reactor in the same dewar of refrigerant.

The inlet system extended into the ion source region of the mass spectrometer such that a fraction of the cold gas molecules emitted from the inlet port were immediately ionized. Therefore, if a reaction product condensed in the reactor exerted a stable vapor pressure of at least 5×10^{-3} mm Hg in the temperature range 77° to 300°K , it could then be transferred from the reactor to the ion source without warm-up above the reactor temperature. In this manner, compounds stable only at temperatures below room temperature could be identified.

The reaction of hydrogen atoms with nitric oxide followed by a rapid quench to 77°K produced only small amounts of nitrous oxide and water. The expected intermediate, HNO, was not detected; however, the presence of nitrous oxide and water indicated that HNO was produced during the reaction process (72). The failure to stabilize and detect HNO is supported by a concurrent study made by Robinson (80).

The reaction of oxygen atoms with ammonia at room temperature produced nitric oxide as the main reaction product. When quenched to 90°K , the conversion to nitric oxide was reduced and several other products were formed. The products were nitrous oxide, diimide, hydrazine, hydroxylamine, water, and ammonium nitrate. The ionization potential of diimide was measured to be 9.8 ± 0.2 eV in agreement with an earlier measurement by Foner and Hudson (14). The identification of diimide demonstrated the capability of the cryogenic inlet system to detect species

stable only below room temperature. The detection of nitric oxide in the products condensed to 90°K indicated that the low temperature quenching was not fast enough to completely arrest the formation of the final products which are observed without quenching.

The reaction of oxygen atoms with ethane followed by a rapid quench to 90°K produced small amounts of ethanol as the only reaction product. This is an example of a successful attempt to stabilize the initial reaction product by low temperature quenching. The reaction probably occurred by an insertion of an excited ^1D oxygen atom into the carbon-hydrogen bond.

The reaction of oxygen atoms with ethylene followed by a rapid quench to 90°K produced carbon dioxide, formaldehyde, acetaldehyde, ethylene oxide, methanol, water, and formic acid. The presence of relatively large amounts of ethylene oxide supported a proposal by Cvetanovic that the initial reaction product was an energy-rich ethylene oxide molecule. The increased quantities of ethylene oxide produced in the present work was a result of the low temperature quenching. The presence of the formaldehyde, methanol, and formic acid suggested that molecular oxygen was also present in the reaction zone.

The reaction of atomic oxygen with acetylene followed by a rapid quench to 90°K produced carbon dioxide, glyoxal, formic acid, water, a red compound or complex disappearing at -123°C , and a white solid which slowly changed to a yellow and finally to a brown color on exposure to the atmosphere at room temperature. The red substance was tentatively explained in terms of a charge transfer complex between unreacted acetylene and formic acid. The room temperature solid was not identified but

was found to contain functional groups of aldehydes and esters. The expected initial reaction product, ketene, was not detected.

The results obtained from the study of these five reactions indicated that, depending on the molecular complexity and energetics of the initial reaction products, a variety of intermediates could be stabilized by low temperature quenching. Subject to the requirement that a compound had to exert a finite stable vapor pressure for mass spectrometric detection, the cryogenic inlet system operated according to design expectations.

CHAPTER I

INTRODUCTION

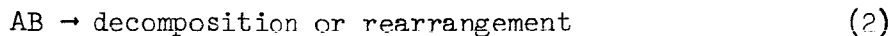
General Problem

A great amount of the work currently being conducted in the field of chemical kinetics consists of determining the series of individual steps, i.e., the mechanism by which chemical reactions occur. In some cases, the detection of compounds intermediate between reactants and final products can give evidence as to the steps involved in the mechanism. The direct detection of the intermediate compounds is often difficult since these species usually possess a large amount of excess energy and consequently have a very transitory existence at normal reaction temperatures. One approach to this difficulty is to carry out the reactions in or near a cryogenic environment. The initial reaction products might then be stabilized and perhaps isolated by this immediate quenching to low temperatures.

Early Approach to Problem

An example of this approach can be seen in the work of Geib and Harteck during the early 1930's (1). Geib and Harteck reacted several simple compounds with hydrogen and oxygen atoms in a reactor immersed in liquid air or liquid oxygen. The reactions they were studying can be represented by the following general equations:





In these equations, A is the atom of hydrogen or oxygen, B is the second reactant, and M is a third body which might be any gaseous species present in the reactor, or the cold wall of the reaction vessel. Reaction (1) is an addition in which the third body M carries off the excess energy of reaction. Reaction (2) might occur on warming to room temperature or if AB is not quenched to a sufficiently low temperature for stabilization. Reaction (3) is an atom abstraction which Geib and Harteck hoped to suppress by carrying out reaction (1) in or near a cryogenic environment.

They report that the reaction of hydrogen atoms with gaseous nitric oxide produced a yellow substance which explosively decomposed on warming to room temperature to form nitrous oxide and water. From the amount of the decomposition products, they suggested the empirical composition of the yellow substance to be $(\text{HNO})_n$.

Geib and Harteck reacted oxygen atoms with several hydrocarbons, two of which were acetylene and ethylene. With acetylene, the reaction products condensed at 90°K formed a mass of yellow to red unstable compounds. After warming to room temperature, the products glyoxal, formic acid, water, carbon monoxide, and carbon dioxide were identified. The reaction of oxygen atoms with ethylene at 90°K produced a colorless solid which began to foam when warmed to 163°K . At room temperature, ethylene oxide, formaldehyde, carbon monoxide, and acetaldehyde were detected.

Geib and Harteck also found that oxygen atoms would react with ammonia to form an intensely yellow deposit at 90°K . They suggested that

the yellow compound might be HNO or NH_3O . At room temperature, water, nitrogen, and a series of oxidation products of ammonia were identified.

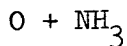
In the experiments just described, Geib and Harteck used cryogenic techniques in their attempts to stabilize the initial reaction products. However, they were unable to extend the use of their cryogenic techniques to the identification of the unstable low temperature reaction products. The analytical equipment then available could only be used near room temperatures. As a result of this lack of cryogenic analytical equipment, one could merely note the appearance of the low temperature reaction products, describe their behavior on warming, and then attempt to relate the conjectured low temperature reaction products to the compounds identified at room temperature.

Purpose of Research

It was obvious that Geib and Harteck's work would have had more significance if they had been able to characterize the products at the low temperatures. The need for low temperature analytical equipment was apparent and this now leads to a statement of the purpose of this research. This research actually had the three following goals: (1) a system in which low pressure, low temperature reactions could be carried out was to be designed and constructed, (2) analytical equipment capable of identifying reaction products which might only be stable at temperatures lower than room temperature was to be developed, and (3) the reaction system and analytical equipment would be used to investigate some of the early reactions described by Geib and Harteck.

Reactions to be Studied

The specific systems to be studied were the reactions of oxygen atoms with ammonia, acetylene, ethylene, and ethane, and the reaction of hydrogen atoms with nitric oxide. As will be noted in the following discussion, since the early work of Geib and Harteck, cryogenic techniques have rarely been used in the investigations of these reactions. The following literature reviews on the atomic reactions are complete to March, 1966.



Since the work of Geib and Harteck, the reaction of atomic oxygen with ammonia has been studied by three groups of investigators. Moore and coworkers (2) combined ammonia and a stream of discharged oxygen at room temperature and at pressures of 0.5 to 1.0 mm Hg and studied the resulting reaction with a medium quartz spectograph. They report the appearance of bands of NH and OH in emission, and they attributed the OH emission to water present as an impurity in the oxygen. Bands of NH_2 could have been masked by the overlapping emission of the air afterglow. In criticism of this work, it should be noted that Geib and Harteck reported water as a reaction product, and hence the OH bands could have resulted from water formed during the reaction, from water present as an impurity, or from free OH radicals.

Avramenko and coworkers (3,4) reacted oxygen atoms and ammonia in the temperature range $348^\circ\text{--}458^\circ\text{K}$ and at pressures of 4, 8.5, and 15.5 mm Hg. They condensed the reaction products to 77°K at some unreported distance downstream from the reaction zone. This distance apparently was great enough to allow the reaction to go to completion because no likely

reaction intermediates were detected in the product mass condensed in the trap. Qualitative tests were made for hydrazine, hydroxylamine, nitrite (from NH_4NO_2), hydrogen peroxide, and oxides of nitrogen. A positive test was only obtained with the nitrite analysis. One point which should be mentioned is that Avramenko and coworkers coated the reactor walls with potassium chloride in an attempt to destroy the OH radicals. They reported that this coating permitted the attaining of reproducible results, however, they did not mention what results were obtained before the use of the KCl.

Wong and Potter (5) reacted oxygen atoms with ammonia in a stirred reactor at temperatures ranging from 350° to 600°K and at a pressure of 0.8 mm Hg. The reaction products were analyzed by use of a time-of-flight mass spectrometer and it was found that NO, H_2O , and small amounts of atomic and molecular hydrogen were produced. They postulated that the nitric oxide and atomic hydrogen were formed by the reaction.



In related studies of ammonia-molecular oxygen flames (6,7) emission bands due to NH_2 , NO, and OH have been observed. These results suggest that many of the same free radical reaction intermediates are involved in both the atomic and molecular oxygen reactions.

In other related studies, it has been found that the combination of ammonia and molecular oxygen will yield varied reaction products which depend on the experimental conditions and/or the type of catalyst being used. If an ammonia-oxygen flame is allowed to impinge upon the surface of cold water (8) or if the reaction products are cooled very rapidly (9),

hydrazine is formed. Hydroxylamine, a proposed intermediate in the oxidation of ammonia (10), can be produced by passing a mixture of ammonia and oxygen over a platinum catalyst heated to 1250°C (11). Ammonium nitrate can be produced by passing an ammonia-air mixture over alkaline catalysts activated with heavy metal oxides at temperatures of 350°C (12).

As will be seen in a later section of this thesis, some recent work on a decomposition product of hydrazine and of hydrazoic acid, diimide, is directly related to the atomic oxygen-ammonia reaction. Diimide has often been suggested to exist as an unstable reaction intermediate (see discussion by Corey, Mock, and Pasto (13)), but only recently has it been definitely detected (14, 15, 16, 17, 18). Using a mass spectrometer which had been modified to detect free radicals and other unstable species, Foner and Hudson (14,15) detected diimide in the gaseous products from an electrodeless electric discharge through a stream of hydrazine or hydrazoic acid vapor. They attributed an increase in ion intensity at m/e (mass/charge) = 30 to be caused by diimide. To confirm this, they passed partially deuterated hydrazine, $N_2H_2D_2$, through the discharge. They observed ion intensity increases at m/e values of 30, 31, and 32 which correspond to $N_2H_2^+$, N_2HD^+ , and $N_2D_2^+$.

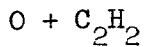
To insure that the peak at $m/e = 30$ was not due to a cracking fragment from hydrazine, Foner and Hudson measured the appearance potentials of the ions at $m/e = 30$ caused by diimide and hydrazine. They found that diimide had an ionization potential of 9.85 ± 0.1 ev, $I(N_2H_2)$, and the $N_2H_2^+$ ion from hydrazine had an appearance potential of 10.98 ± 0.02 ev, $A(N_2H_2^+)$. Dibeler, Franklin, and Reese (19) also measured the appearance potential of the ion at $m/e = 30$ from hydrazine and reported a value of

11.9 ± 0.2 ev. Although this is in disagreement with the value reported by Foner and Hudson, the disagreement is in the direction which does not affect this assignment of the lower energy as being $I(N_2H_2)$.

Foner and Hudson also found that the discharged products from either hydrazine or hydrazoic acid formed a deposit of yellow and white crystals when condensed in a liquid nitrogen trap. The deposit vaporized as diimide, nitrogen, and ammonia and since these three compounds all apparently vaporized at the same time, Foner and Hudson suggested that the vapor pressures of diimide and ammonia should be similar. Using Foner and Hudson's equipment, Blau and coworkers (16,17) detected diimide by mass spectrometry and also by its gas phase infrared spectrum. They repeated the hydrazine experiment described by Foner and Hudson and confirmed the trapping of the yellow product at $86^\circ K$. On warming, the color of the deposit gradually changed from yellow to white along with an increase in system pressure. During this warm-up, diimide, ammonia, and nitrogen were detected in the mass spectrometer with a maximum rate of evolution of diimide at about $160^\circ K$. The nitrogen and hydrazine (which was evolved later) were apparently formed as a result of the reaction of two molecules of diimide. The intensity of the yellow color increased with the diimide concentration, and the yellow deposit was stable for several hours at $120^\circ K$. From their gas phase infrared absorption analysis, they attributed bands at 1277, 1294, 1314, 3050, and 3190 cm^{-1} to diimide.

Rosengren and Pimentel (18) photolyzed hydrazoic acid labeled with deuterium and ^{15}N in solid nitrogen at $20^\circ K$. They identified the absorptions of the photolysis products as those of trans- N_2H_2 (1286 cm^{-1}), trans-HNND (1481 and 1058 cm^{-1}), trans- N_2D_2 (946 cm^{-1}), and cis- N_2H_2 (3074 and

1279 cm^{-1}). This work is in agreement with the results obtained by Blau and coworkers and indicates that their gas spectrum is due to diimide.



This reaction occurs with the formation of a characteristic chemiluminescence which is produced by the excited radicals C_2 , CH , OH , and CHO (20,21). Since it had been shown (22,23) that the radiation from the atomic flames is not greatly different from premixed flames of acetylene and oxygen, Krishnamachari and Broida (24) made a study of the effect of molecular oxygen on the emission spectra of atomic oxygen-acetylene flames.

The mixture of the atomic oxygen-acetylene was first reacted in a molecular oxygen free system. The atomic oxygen was obtained from the "titration" of discharged nitrogen with nitric oxide according to the reaction.



The nitrogen atoms were produced in a 2450 Mc electrodeless discharge and then mixed with nitric oxide. The system pressure was varied from 0.75 to 2.5 mm Hg and the feed gases were introduced at room temperature.

In this study, Krishnamachari and Broida found that the most striking effect of the addition of molecular oxygen to the reaction flame was the large increase in the OH emission and the decrease of CH and C_2 emission. They suggested that this can partly be accounted for by the following reaction of molecular oxygen with a presumably excited CH radical,



Fontijn and coworkers (25,26) carried out similar studies and reached essentially the same conclusions as Krishnamachari and Broida. They reported that the added oxygen acts as a free radical scavenger (27) and leads to the increase of OH radiation as given in Equation (6).

Fontijn and coworkers also reported that the added molecular oxygen gives rise to a downstream increase in light emission. Their explanation for this is that the oxygen molecules, in removing hydrocarbon free radicals, remove ready reaction partners for the oxygen atoms. The resulting increase in downstream oxygen atom concentration causes an increase in the downstream oxygen atom-hydrocarbon reactions. This is a significant observation since it indicates that the oxygen atoms are removed not only by the initial reaction with the acetylene molecules but also by subsequent reactions with the initial reaction products.

In studying the atomic diffusion flame with a mass spectrometer, Fontijn and coworkers noticed the appearance of masses heavier than ketene (the assumed initial reaction product). They did not identify the masses but reported that they all had intensity versus distance profiles which maximized at points well downstream. It was suggested that the masses resulted from ion-molecule polymerization reactions or charge exchange reactions involving already polymerized molecules.

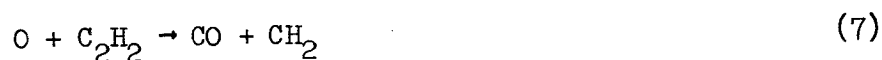
Sullivan and Warneck (28) used a mass spectrometer coupled to a fast flow system to study the atomic oxygen-acetylene reaction. The oxygen atoms were produced by subjecting a 10:1 mixture of helium and oxygen to a microwave discharge or by use of the previously described

nitric oxide titration technique (Equation (5)). They found that carbon monoxide was the major reaction product along with smaller amounts of hydrogen and water. From their results, Sullivan and Warneck decided that the reaction between oxygen atoms and acetylene involved the reactants in a 1:1 ratio.

With a 1:1 ratio of acetylene to oxygen atom concentration, they found that about 1.5 times as much carbon monoxide was produced as the amount of acetylene consumed. As previously concluded by Fontijn and co-workers, Sullivan and Warneck used this fact to conclude that oxygen atoms are consumed in one or more subsequent reactions after the initial reaction with acetylene.

In considering the possible reaction partners for the excess oxygen atom consumption reported by Sullivan and Warneck, it should be noted (29,30) that methylene reacts considerably faster with many other species than with molecular oxygen. Therefore, the reaction of oxygen atoms with methylene should be a likely consideration.

Sullivan and Warneck proposed that carbon monoxide was a direct product of the $O + C_2H_2$ reaction in the equation

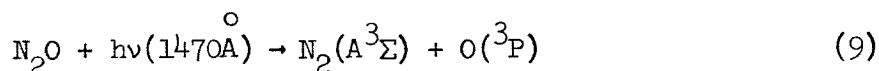


Fenimore and Jones (31) first proposed reaction (7) as a result of their studies with premixed flames of oxygen and acetylene. They suggested that an energy-rich intermediate, $C_2H_2O^*$, would be formed according to



which would then dissociate to form methylene and carbon monoxide.

Haller and Pimentel (32) photolyzed nitrous oxide at 20°K in a solid argon matrix containing acetylene. The low temperature inert matrix was used to confine and stabilize the primary reaction products. The photolysis lamp emitted mainly at 1470 Å, and it had previously been shown (33) that this photolysis produces ground state oxygen atoms according to



Infrared spectra showed that reaction occurred with acetylene to produce an absorption at 2143 cm⁻¹. After comparing this value with the absorption produced by gaseous ketene (2151 cm⁻¹) and allowing for the gas-solid absorption shift, Haller and Pimentel concluded that the low temperature reaction product was ketene. This identification of ketene supports the reaction proposed by Fenimore and Jones since it is known (34) that energy-rich ketene will decompose to yield carbon monoxide and methylene.

The oxidation of acetylene has also been studied in shock tube experiments involving sudden applications of high temperature and pressure (35,36,37). Oxygen atoms are proposed to react with acetylene as,

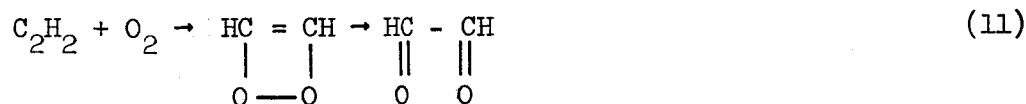


This hydrogen-abstraction reaction is endothermic by about 0.5 ev (38) and can probably be ruled out for the room temperature reaction. Therefore, if reaction (10) is occurring, the shock tube oxidation studies should not be relevant to the low temperature, low pressure study in this thesis.

The oxidation of acetylene by molecular oxygen has been studied under various conditions of temperature and pressure by a number of investigators (see reviews by Minkoff and Tipper (39) and by Shtern (40)). Many mechanisms have been proposed to explain the resulting reaction products and since the issue is still unsettled, only the most recent work of Hay and Norrish (41) will be mentioned.

Hay and Norrish studied the oxidation reaction in a static system under varying conditions of temperature, pressure, ratio of oxygen to acetylene, surface condition, reactor diameter, and addition of formaldehyde, glyoxal, and inert gas. The course of the reaction was followed by pressure change and by product analysis. The main reaction products were found to be carbon monoxide, carbon dioxide, and water with smaller amounts of hydrogen, glyoxal, formaldehyde, and formic acid. Trace amounts of acetaldehyde, acrolein, glyoxalic acid, oxalic acid and hydrogen peroxide were also found.

From the analysis of their experimental results, Hay and Norrish reached the conclusion (first suggested by Semenov (42)) that the oxidation of acetylene was a degenerately branched chain reaction. Glyoxal was taken to be the intermediate responsible for branching as given in the two following initiation and branching reactions:

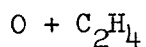


Their complete mechanism will not be reproduced, but it should be mentioned

that the reaction of oxygen atoms is not considered in the proposed mechanism.

Bone and Carruthers (43) reported the formation of an unidentified oily phenolic compound from the slow combustion of acetylene. They postulated that it was formed by the polymerization of an initially formed hydroxy-acetylene.

The polymerization of acetylene, often in the presence of oxygen, has been accomplished through the use of many activators (heat, chemical reagents, electric discharge, light, cathode rays, alpha particles, etc.) and a review of the work has been written by Egloff, Lowry, and Schaad (44). As an example, Marshall (45) exposed acetylene gas to cathode rays and found that a fluffy white-yellow powder deposited on the chamber walls. The temperature was increased during the reaction and the product changed in color from light yellow to chocolate-brown. Marshall observed that the polymer would take up about 30 percent of its weight of oxygen on standing in air. The identity of the polymer was not established.

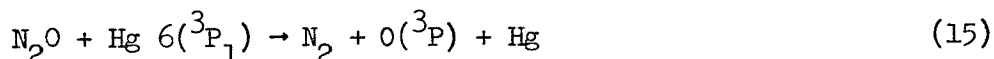


This reaction has been studied in most detail by groups in Russia (46,47) and Canada (48,49,50,51,52). The Russian investigators, Avramenko and Kolesnikova, generated oxygen atoms by the electric discharge technique and studied their reactions with ethylene from 70° to 150°C. In a sketchy product analysis they reported the formation of acetaldehyde, formaldehyde, formic acid, carbon monoxide, and carbon dioxide with formaldehyde as the principal product. From this product analysis, Avramenko and Kolesnikova concluded that the initial reaction between an oxygen atom and an ethylene molecule broke the carbon-carbon double bond with the

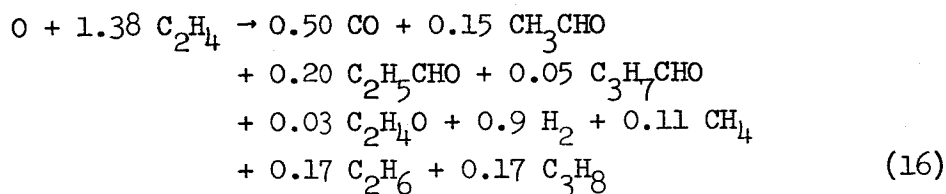
formation of formaldehyde according to the equations



During the year (1955) in which the first Russian paper appeared, Cvetanović, the head of the Canadian research group, published a paper (49) in which he directly disagreed with the conclusions reached by the Russians. Cvetanović reacted oxygen atoms and ethylene in a molecular oxygen-free system at room temperature and at 123°C, and in a pressure range of 20 mm to 250 mm Hg. The oxygen atoms were produced in the ground triplet state (53) by the mercury photosensitized decomposition of nitrous oxide,



The reaction products were identified by mass spectrometry and by gas-liquid partition chromatography. Cvetanović reported the following stoichiometric equation:



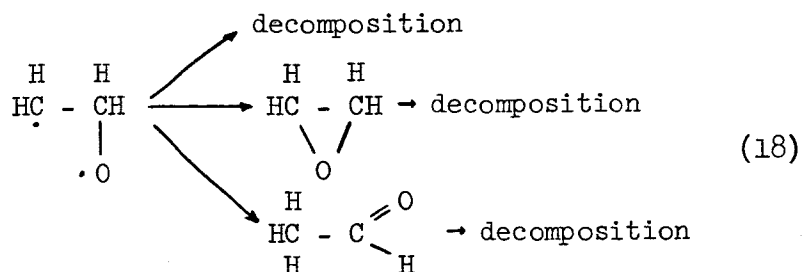
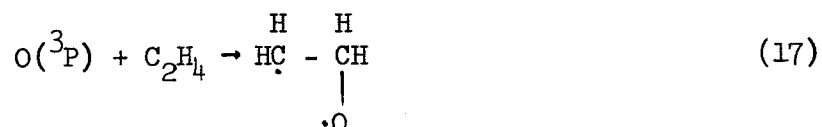
Only a trace of formaldehyde was detected at 123°C which is to be contrasted with the apparent larger yield reported by Avramenko and Kolesnikova. As will be seen, the formation of the formaldehyde was a result of the presence

of molecular oxygen in the electrical discharge system.

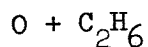
In another experiment, Cvetanović determined the effect of adding molecular oxygen to the system. He found that there was a large increase in the rate of carbon monoxide formation while ethane and hydrogen were eliminated and the amounts of methane and aldehydes greatly reduced. Large quantities of new compounds (formaldehyde, formic acid, alcohols, and water) were formed and Cvetanović attributed their formation to the interaction of molecular oxygen with the free radicals formed in the primary reaction process.

Although only a small amount of ethylene oxide was formed, Cvetanović postulated that the primary process involved in the reaction of ^3P oxygen atoms with ethylene was the direct addition of the atom to the double bond. This would form an energy-rich molecule ($\text{C}_2\text{H}_4\text{O}^*$) which might decompose in much the same manner as a normal ethylene oxide molecule which had absorbed a large amount of energy. In support of his proposal, Cvetanović found that the same type of products were formed in the mercury sensitized decomposition of ethylene oxide and in the reaction of oxygen atoms with the ethylene.

The reaction process was represented (51) by the equations



In further studies of higher alkenes (50), Cvetanović found that larger quantities of epoxides were formed with a corresponding decrease in fragmentation products. This change was attributed to the increased capability to absorb the excess energy of reaction.

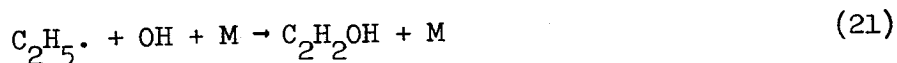


Harteck and Kopsch (54) first investigated this reaction at room temperature. They reported that bands due to hydroxyl were emitted and the main products were carbon dioxide and water.

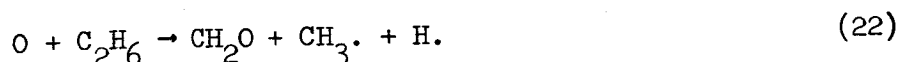
Much later, using a flow system, Avramenko and Kolesnikova (55,56) combined ethane with oxygen atoms from a discharge tube, and condensed the reaction products at 77°K. However, the trap was located at such a distance from the reaction zone that no unstable product would have likely survived the trip downstream. The reaction products were ethanol, formaldehyde, carbon monoxide, carbon dioxide, and a trace of acetaldehyde. They proposed that the ethanol was formed by the insertion reaction



or by the two step abstraction-recombination reactions



where M is a third body required to carry off the excess energy. They also proposed the following reaction for the formation of formaldehyde



In a paper presented at the Tenth International Symposium on Combustion, Wright (57) suggested a new mechanism for the reaction of oxygen atoms with alkanes. According to his mechanism, the main reaction appeared to be a displacement of two groups on a single carbon atom of the parent hydrocarbon by the oxygen atom with the attendant formation of a carbonyl bond. This was in contrast with the former mechanism of hydrogen abstraction and subsequent radical reactions. Wright produced ground state atoms by the titration technique (Equation (5)), and reacted them with several alkanes at 30°C and at 7.6 mm Hg total pressure. For all alkanes above ethane, a considerable amount of acetone was formed as a reaction product. To account for this formation of acetone by the hydrogen abstraction mechanism, Wright developed a five-step reaction sequence involving three separate encounters with atomic oxygen. This appeared to be highly improbable, and therefore Wright rejected the hydrogen abstraction mechanism in favor of his new mechanism.

As an aid in comparing Wright's results with those of others, it is important to contrast his final products with those reported by other investigators. With ethane, Wright reported the formation of formaldehyde, acetaldehyde, and water as main products. With propane, the main products were acetaldehyde, acetone, propylene, ethylene, and water.

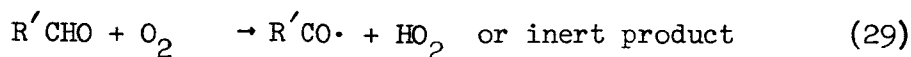
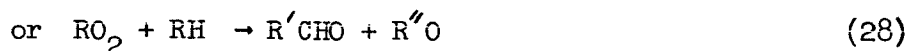
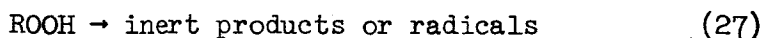
Yamazaki and Cvetanovic (58) selectively produced ground state triplet oxygen atoms (3P) and excited state singlet oxygen atoms (1D) and reacted them with propane at room temperature and in a pressure range of 400 to 6400 mm Hg. They found that the singlet oxygen atoms reacted by an apparent insertion action to form alcohols or products which could be traced to alcohol fragmentation. The triplet oxygen atoms reacted

to form products which were attributed to an abstraction mechanism. The abstraction products were 2, 3 - dimethylbutane, 2 - methylpentane, and n-hexane. In contrast to the results of Wright, no ethylene, acetone, or propylene were detected.

Since the two reactions of oxygen atoms with propane produced greatly contrasting results, it is apparent that further work is necessary before the new mechanism proposed by Wright can be fully evaluated. Although the work by Wright and by Yamazaki and Cvetanović was not specifically directed to ethane, the results are important for purposes of this thesis since they can be applied to alkanes in general.

It is appropriate here to mention briefly the proposed mechanisms for the reaction of ethane (or alkanes in general) with molecular oxygen. Semenov (42) established that the gaseous phase slow oxidation of hydrocarbons could be represented by a chain reaction which proceeded with degenerate branching. During the chain process an intermediate was formed which possessed the ability to give free radicals with greater ease than the original hydrocarbon. The identity of the intermediate responsible for the degenerate branching is still a subject of much controversy. Walsh (59) and Hinshelwood (60) postulated that hydroperoxides were the intermediates responsible and in later work, Norrish (61) proposed that aldehydes were the intermediates responsible for the degenerate branching. Since the issue is still unresolved, both schemes are represented in the following equations where R denotes an alkyl radical.





Equations (26) and (27) are representative of the peroxide mechanism and equations (28) and (29) are taken from the proposed aldehyde mechanism.

H + NO

Smallwood (62) investigated the recombination of hydrogen atoms due to the addition of nitric oxide and found that almost all the nitric oxide was recovered unchanged. As previously described, Geib and Harteck (1) reported the formation of a yellow explosive material on condensing the reaction products to 77°K. Taylor and Tanford (63) carried out a mercury sensitized reaction between hydrogen and nitric oxide at 100°C and reported the formation of nitrogen and water. They postulated a mechanism based on the production of HNO molecules to explain their data.

Dalby (64) first identified HNO spectroscopically in the gas phase using flash photolysis of ammonia in the presence of nitric oxide. Evidently, the photolysis of ammonia produced NH_2 radicals and hydrogen atoms which then reacted with the nitric oxide. The electronic absorption spectrum of HNO was observed in the region 6500-7700 Å.

Robinson and McCarty (65,66) condensed HNO in an argon matrix at 4°K and after allowing for the gas-solid spectrum shift, confirmed the

electronic spectra for HNO earlier reported by Dalby. The HNO was produced by passing a 1:25 mixture of hydrazine and argon through a 15 Mc electrodeless discharge. The oxygen was obtained from the water impurity which was not removed from the hydrazine. The product was collected on a cold finger which was placed close enough to the discharge region so that secondary gas phase reactions could be avoided before condensation.

Brown and Pimentel (67) photolyzed methyl nitrite in an argon matrix at 20°K and found that the primary products were formaldehyde and nitroxyl, HNO. The detection of HNO by its infrared spectrum was confirmed by the band shifts occurring upon deuteration. From a consideration of force constants and other molecular parameters of related molecules, Brown and Pimentel were able to conclude that nitroxyl possessed a normal double bond and had the structure HNO rather than HON. They also report that the HNO angle is near 110°, which is somewhat larger than Dalby's earlier estimate of 102° (64).

The emission spectra of HNO was studied by Cashion and Polanyi (68) and by Clement and Ramsay (69). Both groups reacted hydrogen atoms with gaseous nitric oxide and reported similar emission bands. Clement and Ramsay found that the radiation emitted by the reaction was not visible. They also reported the occurrence of predissociation of the molecule in the excited state and estimated the upper bound for the dissociation energy to be 48.6 Kcal/mole.

Clyne and Thrush (70,71) reacted hydrogen atoms and nitric oxide in a flow system at room temperature and in a pressure range of 0.8 to 4 mm Hg. By measurement of the intensity of the feeble red glow due to emission by HNO, they studied the kinetics of the reaction. They suggest

that the reaction mechanism was



where M is a third body, followed by the rapid reaction



In further work, Clyne (72) determined that reaction (31) accounted for 99.9% of the removal of HNO and the following reaction accounted for 0.1% of the removal of HNO



Harvey and Brown (73) passed a 1:1 mixture of argon and hydrogen through a discharge tube at a pressure of 200 microns and combined the discharged gas with a stream of nitric oxide to yield a mixture having a partial pressure of nitric oxide of 10 microns. The resulting gas mixture was condensed to liquid helium temperature. Infrared spectra of the condensed solids confirmed the previous assignments of the NO stretching and HNO bending modes.

CHAPTER II

APPARATUS AND EXPERIMENTAL TECHNIQUES

The experimental apparatus was designed to fulfill two main requirements: (1) low pressure exothermic reactions of atomic oxygen or hydrogen with several compounds had to be carried out in the immediate vicinity of a low temperature environment, and (2) analytical equipment had to be connected to the reaction chamber in such a manner that all quenched products could be identified, even if some of the products were only stable at cryogenic temperatures. These requirements were met, and a description of the apparatus is given in the following sections.

General Reaction System

A schematic diagram of the reaction system is shown in Figure 1. The gas to be dissociated, either hydrogen or a 3:1 mixture of helium and oxygen, entered the system by passing through a rotameter at a known constant pressure. The gas entered the region of the discharge coil where partial dissociation and excitation occurred and then continued around a 90 degree bend to approach the U-tube reactor. The stream of molecular and atomic species was mixed with a gaseous stream of the second reactant at a point 15 mm above the bottom curved surface of the U-tube reactor. The second reactant (ammonia, nitric oxide, acetylene, ethylene, or ethane) also entered the system by passing through a rotameter at a known constant pressure.

The resulting mixture of reaction products and unreacted gases

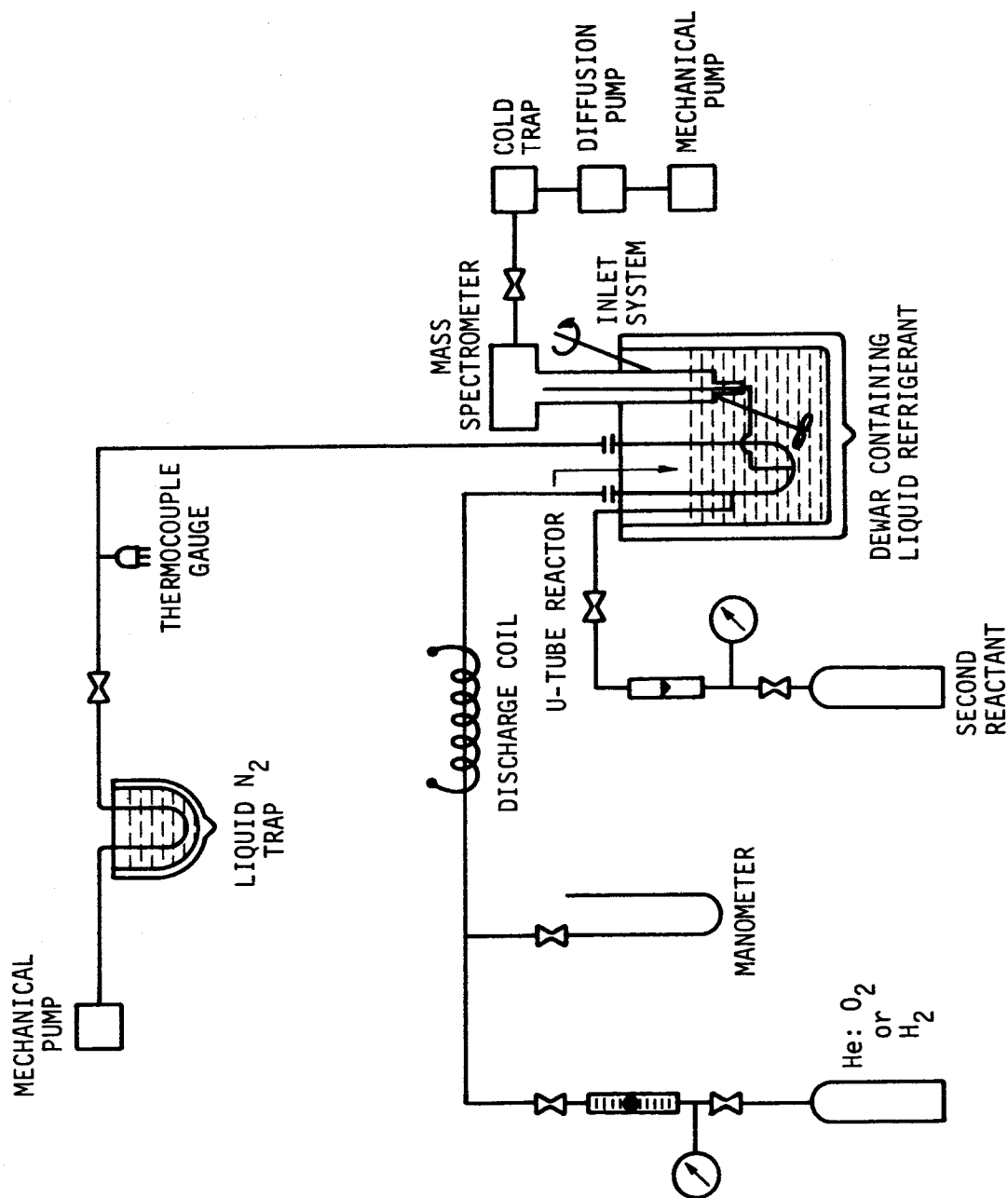


Figure 1. Schematic of Reaction and Analytical System.

collided with the cold walls of the reactor (usually 77° or 90°K) where all condensables were trapped. Noncondensables were continuously removed from the reactor by a vacuum pump. As shown in Figure 1, the reactor was connected to a mass spectrometer through an unusual inlet system. As will be described in more detail in another section of this chapter, this arrangement of analytical equipment permitted the identification of all reaction products, regardless of their stability at or below room temperature.

The vacuum pump used with the reaction system was a Welch Duo-Seal Model 1405 having a free air capacity of 58 liters per minute. A cold trap was placed in the line between the reactor and vacuum pump in order to prevent reaction product contamination by back diffusion of pump oil. Most of the reaction system was constructed from 10 mm inside diameter pyrex glass tubing; however, the pump-out line from the reactor was enlarged to 18 mm inside diameter to reduce the resistance to flow and therefore increase the pumping speed in the reactor. When no leaks were present, the system could be evacuated to pressures of 10^{-3} mm Hg. The system pressure was measured in the range 10^{-3} to 1 mm Hg with a Vacuum-Electronic Engineering Company thermocouple gauge, type DV-1M, and control unit type DG2-2T. Higher pressures were measured with a mercury manometer. During reaction, the usual system pressure was in the range 0.5 to 2.5 mm Hg.

Gas Purification

The hydrogen contained small amounts of oxygen and water vapor which caused the formation of contaminating reaction products. The oxygen was removed by passing the hydrogen through a packed tube containing

palladium asbestos heated to 400°C or a packed tube containing copper turnings heated to 800°C. These packed tubes were heated by a 422 watt electric furnace. The water vapor was removed by subsequently passing the hydrogen through a liquid nitrogen trap.

The nitric oxide was obtained from the Matheson Company and had a purity of 98.5%, the balance essentially being nitrogen dioxide. Since nitrogen dioxide freezes at -9°C and has a vapor pressure of 1 mm at -55.6°C, while nitric oxide freezes at -161°C, the nitric oxide was readily freed of NO₂ by freeze-out. The nitric oxide was simply passed through two traps at -155°C (2-methyl pentane freezing point), and then into the U-tube reactor, the impurities being left behind in the traps. Any oxygen present would have reacted to form nitrogen dioxide according to



which readily occurs at room temperature.

After examination with the mass spectrometer, the other gases, all obtained from the Matheson Company, were considered pure enough to be used directly from the cylinders. The ammonia was 99.99% pure and the three hydrocarbons had the following minimum purities: ethane - 99.9%, ethylene - 99.9%, and acetylene - 99.6%. A typical analysis of acetylene reported by the Matheson Company was: C₂H₂ - 99.66%, CO₂ - .04%, O₂ - .04%, N₂ - .14%, and H₂O - .12%. The amount of the impurities present should not have affected the experimental results; therefore, no purification was attempted.

Production of Hydrogen and Oxygen Atoms

The hydrogen and oxygen atoms were produced by flowing the molecular gas through an electrodeless radio frequency discharge coil. The discharge coil was wound on a pyrex tube of 33 mm outside diameter and was made of fifty turns of 14 gauge copper wire. The discharge was produced in a concentric 12 mm diameter quartz or pyrex tube; compressed air was blown into the annular space to provide cooling. The concentric tube arrangement was necessary to prevent high voltage arc-over from the coil to the plasma resulting in a puncture of the inner tube.

The discharge coil was powered by a Hallicrafter's radio transmitter model HT-4B having a maximum power output of 320 watts. For maximum power transfer and hence maximum production of atoms, the output impedance of the transmitter had to be matched to the impedance of the plasma. Since the impedance of the plasma is a function of the nature of the gas being excited, the gas pressure, and the flow rate, it was necessary to design an impedance matching network having a wide range of operability. This network is shown in Figure 2 where those components enclosed in dashed lines were mounted in a 17 x 13 x 4 inch chassis base which was itself mounted within one foot of the discharge tube. The 52 ohm coaxial lead from the transmitter was 10 feet long. The standing wave ratio (SWR) meter was a type P2 sold by Knight Electronics Company. The two variable air gap capacitors were made by Hammarlund Manufacturing Company.

The output impedance of the transmitter was 52 ohms, and it was therefore necessary to adjust the two capacitors until the impedance of the coil system with its plasma core appeared as 52 ohms. The impedance

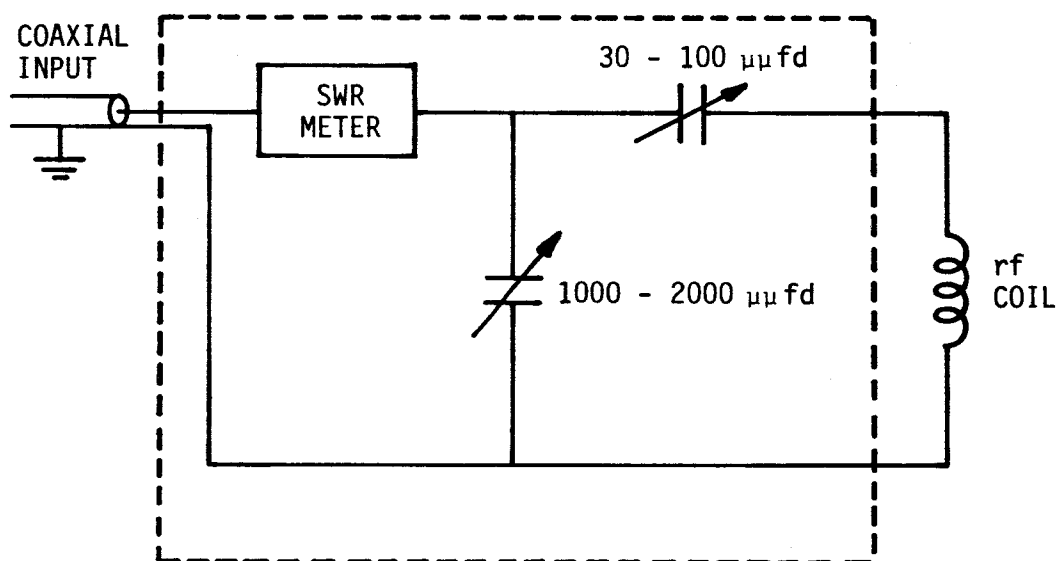


Figure 2. Impedance Matching Network.

match (or mis-match) was indicated by the SWR meter. It was found that with the series capacitor set at $40\mu\text{f}$ and the parallel capacitor set at $2000\mu\text{f}$, the standing wave ratio was usually less than two, and the resonant frequency was approximately 3.5 mcps.

When the discharge coil and matching network were used with the previously described reaction system, it was found that an intense discharge could be maintained up to a pressure of about 80 mm Hg when hydrogen was flowing through the system.

A mixture of excited and ground state atoms, ions, and molecules are produced in the discharge. Calculations have shown that depending on the particular gas and the flow rate, only 5 to 30 percent of the available power from the transmitter is necessary to dissociate the molecules into atoms in excited states. As an example, at the highest He-O₂ flow rate used, only 50 watts were required to excite the helium to the 2^3S state and dissociate the oxygen into atoms in the excited 1D state.

The presence of the hydrogen and oxygen atoms in the reactor at a point 4 feet removed from the discharge was determined by qualitative tests. Hydrogen atoms will react with yellow molybdic anhydride to form blue-grey molybdenum dioxide (74) according to the equation



This test was made periodically during the course of the experimentation and always gave immediate indication of the presence of hydrogen atoms.

Two tests were used for oxygen atoms. The discharged gas was passed through the U-tube reactor immersed in liquid nitrogen, and, if

oxygen atoms were present, blue liquid ozone was formed by the reaction



where M is the cold reactor wall which removes the excess energy of reaction. The second test was based on the greenish-yellow light emission (75) from the reaction



No quantitative tests were made to determine the actual percentage of hydrogen or oxygen atoms at any point in the system.

U-Tube Reactor

As can be seen in Figure 3, the U-tube reactor was simply a modified cold trap. The upper arms were made of 10 mm inside diameter pyrex tubing which then expanded at the U-tube section to 15 mm inside diameter. The upper arms terminated at greaseless, O-ring seal joints. These joints facilitated the removal of the reactor for cleaning and also eliminated the possibility of contamination from reactions of the atoms with grease lubricants.

The second reactant entered, in the position shown in Figure 3, through 1 mm inside diameter capillary tubing. The gaseous sample to the mass spectrometer left the reactor through the line in the middle section of the U-tube. The pyrex line was connected to the metal inlet system by means of a standard 1/4 inch Kovar glass-to-metal seal.

Magnetic Deflection Mass Spectrometer

The magnetic deflection mass spectrometer was chosen as the analy-

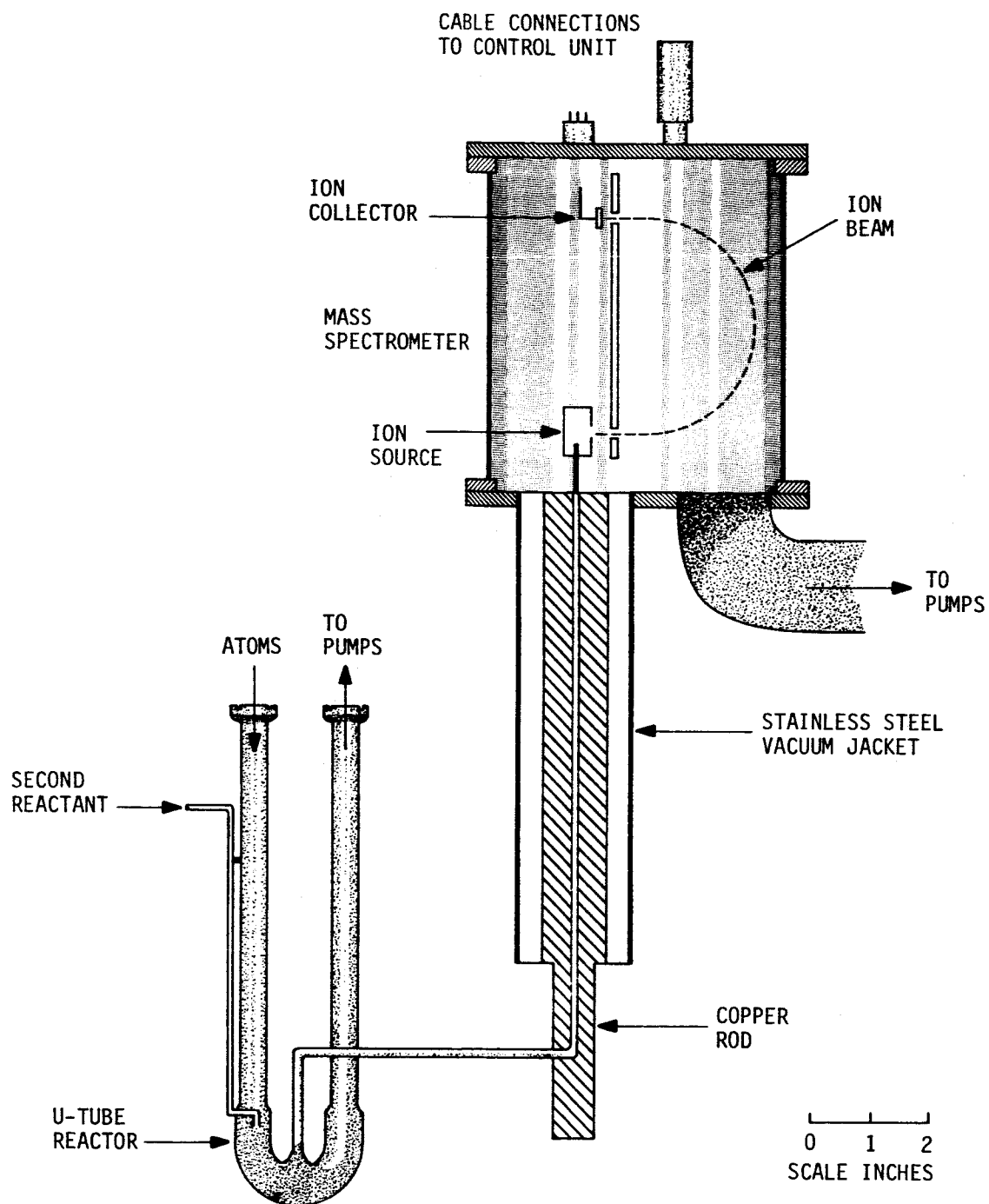


Figure 3. U-Tube Reactor and Inlet System to Mass Spectrometer.

tical instrument for the following reasons. The analyzer tube unit was constructed such that cryogenic equipment could easily be assembled close to the ion source. The data obtained were easily understood, and also, the spectrometer was relatively inexpensive.

It should be emphasized that mass spectrometry is suitable for analysis only if the unknown substance exerts a stable vapor pressure before it is lost either by thermal decomposition or by chemical reaction. It is also true that some systems do not exist in the vapor in the same chemical state as they do in the condensed phase, e.g., N_2O_3 .

The magnetic deflection mass spectrometer was the Model MS-10 manufactured by Associated Electrical Industries of England. The MS-10 detected masses in the range of m/e from 2 to 200. The working pressure was between 10^{-4} and 10^{-10} mm Hg, and the detection limit was claimed to be better than 10^{-10} mm Hg for individual sample components. The ion current for any particular mass could be read on an output meter and it was also possible to attach a potentiometric recorder. The MS-10 had two main components: (1) the tube and magnet assembly (8" x 8" x 13") which contained the ion source and collector, and (2) the electronic control unit. The two components were connected by 10 feet of cable and this separation facilitated the connection of the smaller tube unit to the reaction system.

The vacuum in the mass spectrometer was maintained by the standard fore pump, diffusion pump, and cold trap arrangement. The oil diffusion pump was the Vacronic Laboratory Equipment Company model HUP-150 having a pumping speed of 140 l/second, and was backed by a Welch model 1405 mechanical pump. The cold trap was designed and constructed in this

laboratory. It had a capacity of 0.5 liters and would hold liquid nitrogen for a period of five hours.

The connecting lines were made of short length, large diameter pipe to keep the pumping speed in the mass spectrometer source as high as possible. It was calculated that the connecting lines reduced the pumping speed at the source to a value of about 10 l/second.

The pressure in the mass spectrometer was measured by a Vacuum Electronic Engineering Company discharge gauge, model DG-2-11, and control unit type DG 2-2T.

Cryogenic Inlet System

To identify the reaction products condensed in the U-tube reactor, some of which might be stable only at temperatures below room temperature, a cryogenic inlet system was employed to transfer the sample from the reactor to the mass spectrometer. The reactor, inlet system, and mass spectrometer tube unit are shown in Figure 3. The inlet system, i.e., the passageway from the reactor to the spectrometer, was maintained at essentially the same temperature as that of the reactor by immersing both the inlet system and the reactor in the same dewar of refrigerant. This is shown in Figure 1. The temperature gradient from the bottom to the top of the inlet system was minimized by three design considerations: (1) the inlet tube was made from a rod of high thermal conductivity copper, (2) the copper rod was nickel plated to reduce its emissivity and hence its heat gain by radiation, and (3) the pressure in the space around the rod (above the refrigerant) was maintained at 10^{-6} mm Hg to reduce heat gain by conduction and convection. Calculations indicated that a temperature gradient of 1° to 3° K might exist over the length of the inlet tube when

the bottom was immersed in liquid nitrogen. To more thoroughly explore this rather crucial point, a copper-constantan thermocouple was soldered into the upper end of the copper rod, and it was found that a temperature gradient of 3°K was present when the lower end of the rod was immersed in liquid nitrogen. This was the largest gradient which existed, and hence the inlet temperature problem should not have greatly affected the experimental results.

A two inch length of 0.02 inch inside diameter monel capillary tubing which fitted tightly inside a two inch length of specially made copper tubing was placed at the upper end of the copper inlet rod. The capillary tubing extended into the ion source region of the spectrometer so that the gas molecules emitting from the capillary were immediately ionized. This condition of immediate ionization was the most important feature of the apparatus.

It was found that a product partial pressure in the reactor of at least 5×10^{-3} mm Hg was necessary for mass spectrometric detection. This rather high minimum detectable partial pressure was characteristic of the particular system geometry and effective pumping speeds.

Although the gas molecules were transferred from the reactor to the spectrometer without significant warm-up above the refrigerant temperature, the ions had to travel from the ion source to the collector plate in a room temperature environment. The time for this ion transport was important since it represented the minimum ion lifetime necessary for detection. In the magnetic deflection spectrometer, the time required was a function of the mass being accelerated, but it was always of the order of 1 microsecond.

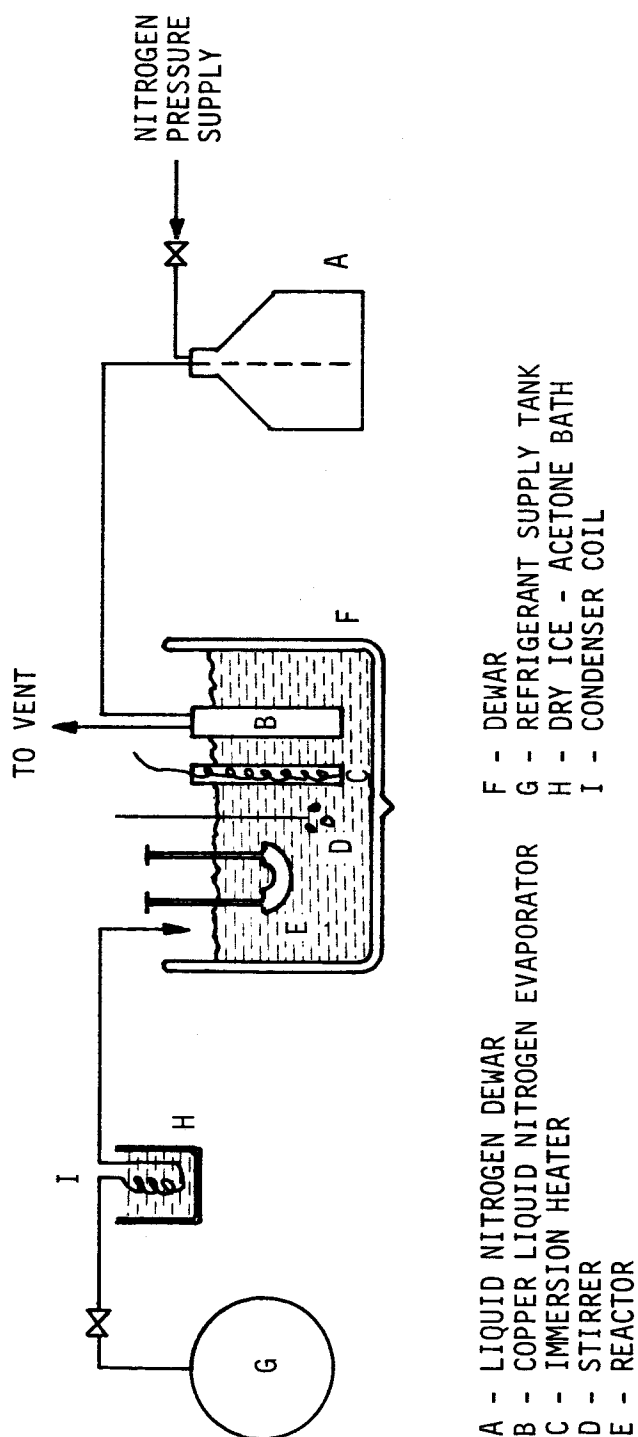
The copper inlet rod was 1-1/4 inches in diameter and 14 inches long. A 1/4 inch hole was drilled through 10 inches of the rod to allow passage of the gases to the mass spectrometer. Between the reactor and inlet system there were 4 inches of 1/16 inch diameter tubing and 4 inches of 1/4 inch diameter tubing which were immersed in the refrigerant during operation.

Temperature Regulation

The low temperatures were produced by surrounding the reactor and inlet system with a dewar of refrigerant which was either liquid nitrogen or liquid oxygen during the early experimentation. When it became necessary to slowly warm the reactor and inlet system, liquid propane or liquid 2-methyl pentane were used as refrigerants. Propane has a convenient liquid range (freezing point to normal boiling point) of 86° to 231°K and 2-methyl pentane has a range of 119° to 333°K .

The refrigerant temperature regulation system is shown in Figure 4. The refrigerants were precooled by initially passing through a copper coil immersed in a dry ice-acetone bath. After the dewar was filled with liquid, the refrigerant was cooled to lower temperatures by using liquid nitrogen. A continuous stream of liquid nitrogen was forced into the copper liquid nitrogen evaporator which was itself immersed in the well stirred dewar of liquid refrigerant. With this arrangement, the refrigerant temperature could be reduced from -60°C to -180°C (using liquid propane) in about 30 minutes.

The temperature could be regulated by the combined manipulation of the power dissipation in the immersion heater and the liquid nitrogen influx to the evaporator. In actual practice, the temperature was only



INLET SYSTEM TO MASS SPECTROMETER NOT SHOWN

Figure 4. Refrigerant Temperature Regulation System.

regulated during the time of reaction. During the warm-up period, the refrigerant temperature increase due to the ambient heat leak was so small that it was not necessary to use liquid nitrogen. Therefore, the mass spectra were recorded as the refrigerant temperature gradually increased. The immersion heater was turned on when it became necessary to increase the rate of temperature rise. The stirrer was used constantly to reduce temperature gradients in the dewar.

Temperatures were measured using a copper-constantan thermocouple and a Leeds and Northrup type 8686 millivolt potentiometer. The stirrer was powered by a 1/100 horsepower motor using a variable powerstat to produce 0 - 5000 RPM. The standard laboratory immersion heater had a maximum output of 400 watts and was enclosed in a quartz tube of 5/16 inches in diameter and 11 inches in length. The amount of heater power was regulated by a variable powerstat. The dewar had a 6 inch inside diameter, a 10 inch depth, and held 4 liters of refrigerant.

Safety Precautions

Propane and 2-methyl pentane are explosive hydrocarbons and several safety precautions were taken. The region of the reaction system in which the dewar of refrigerant was located was completely surrounded by a plexiglas box-like structure. The refrigerant vapors were removed from this structure by a centrifugal blower exhausting into a hood. The stirrer motor was located outside the plexiglas structure. All of the nearby metal was well grounded.

Cryogenic Inlet System to TOF Mass Spectrometer

A Bendix time-of-flight (TOF) mass spectrometer, Model 12-107, equipped with another type of cryogenic inlet system (76) was readily

available, and several experiments were performed to compare the operation and results obtained with the two inlet systems. In addition, energy measurements of high accuracy could be made using the TOF mass spectrometer.

The cryogenic inlet system to the TOF mass spectrometer consisted of two pots which could be independently thermostatted at any temperature in the range 77° to 373° K. The temperature variance was obtained by balancing the flow of liquid nitrogen through the pots with a carefully adjusted power dissipation in heaters wound on the center tubes of the pots. Temperature control was obtained by the use of two Leeds and Northrup Speedomax H recorder-controllers which governed the amount of power dissipated in the heaters.

Both inlet systems were designed to inject gas samples directly into the ionizing electron beam without prior warm-up above the temperature of the refrigerated reactor.

The reactor used in the TOF mass spectrometer experiments is shown in Figure 5. It was constructed of pyrex glass and was connected to the metal inlet system by means of a 19/22 standard taper joint. The reacting mixture of atoms and second reactant (ammonia, nitric oxide, etc.) entered the cold center tube of the inlet system where the condensable products were trapped. As in the experiments with the magnetic deflection spectrometer and inlet system, product identification was made during a controlled warm-up from the quenching temperature.

Methods of Product Identification

After the apparatus had been made operable and the conditions necessary to produce the reactions had been established, the balance of

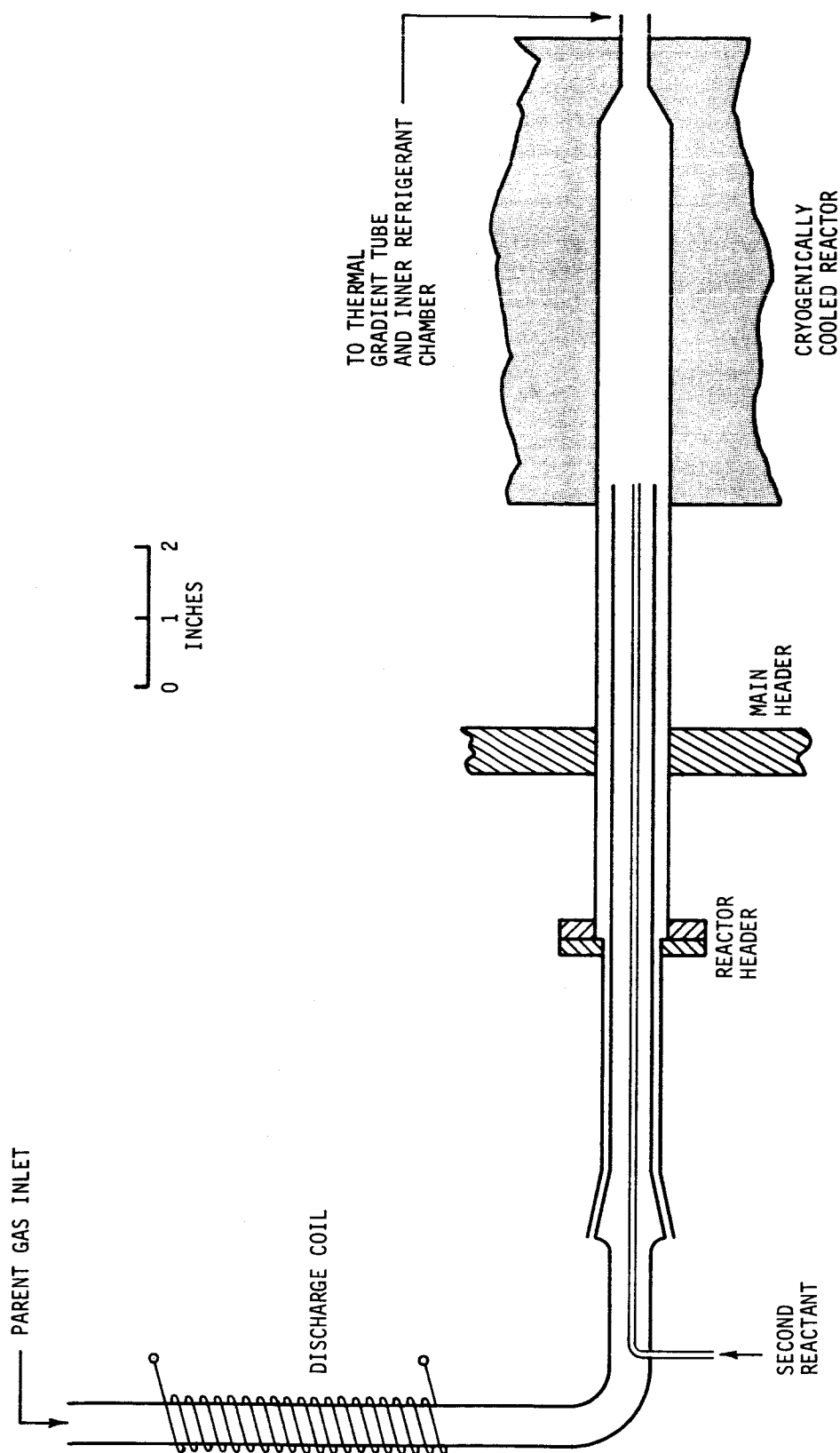


Figure 5. Reactor Used in TOF Mass Spectrometer Experiments.

the experimental work consisted of identifying the reaction products. Four general methods were used separately or collectively for this identification. The methods were: (1) visual observation of the products in the reactor, (2) use of the mass spectrometer in determining the mass cracking patterns, (3) correlation of vapor pressure data with temperature at which maximum product evolution occurred, and (4) use of the TOF mass spectrometer to measure appearance potentials of ions of critical interest.

Visual observation was the only method Geib and Harteck (1) used in identifying the low temperature reaction products from their early study of the same reactions that were studied in this thesis. In the present work, visual observation was used mainly to determine if the reaction seemed to be proceeding, and occasionally as a support for the other methods.

Methods (2) and (3) were used together very extensively in the following manner. The cracking pattern of an unknown reaction product would be determined at some temperature, and a tentative species assignment would be made. During continued warm-up of the reaction mass, the temperature at which maximum evolution of this product occurred would be noted. It is characteristic of this system that maximum evolution of a compound from the reactor occurred when that compound exerted a vapor pressure of 0.1 ± 0.05 mm Hg. Therefore, if the compound tentatively identified using method (2) had a vapor pressure of approximately 0.1 mm Hg at the temperature of maximum evolution, the identification was considered to be correct. Unless otherwise noted, the vapor pressures used in this work were extrapolated from data compiled by Stull (77) and listed in a standard reference source (78). The vapor pressures are

presented in Table 6 in Appendix A.

In those cases where little known and/or normally unstable compounds were present, and also as a support for methods (2) and (3), the TOF mass spectrometer was used to measure the appearance potentials of the parent ion (if present) and certain of its fragments. This use of the mass spectrometer in low temperature chemistry has previously been described in a recent paper from this laboratory (79).

In addition to the general methods listed above, other methods were occasionally used for the identification of low vapor pressure, solid reaction products existing at room temperature. Qualitative tests were carried out on the products when possible. On one occasion, several infrared spectra were obtained in an attempt to identify a polymeric-appearing reaction product.

CHAPTER III

RESULTS AND DISCUSSION

Several types of results were obtained from the present work, the most specific being the numerous reaction product identifications. From these identifications, the operating characteristics of the cryogenic inlet system were defined and the relative quenching efficiencies for the several reactions were determined. From the combination of these results, various implications regarding the detailed chemistry of the reactions have been suggested.

In this chapter, pertinent data, tables, and figures are included to illustrate the discussion. The more detailed raw data are found in Appendix B. For each reaction studied, the raw data presented are representative of several reproducible experiments.

Unless otherwise noted, the heat of formation data that are used in the energetic arguments have been taken from a compilation in a standard reference source (78). Because of the uncertainty in the heats of formation of some of the free radicals, the energy changes are only presented to the nearest kilocalorie.

H + NO

This reaction was chosen for study in hopes of synthesizing weighable amounts of HNO, nitroxyl, at cryogenic temperatures. However, no direct evidence was obtained for the presence of this species. In attempting to identify nitroxyl, both the TOF and magnetic spectrometers

were employed.

Two types of visual indications of the expected formation of HNO had previously been reported. Geib and Harteck (1) reported the formation of a yellow explosive compound at 77°K which they suggested to be HNO, and Clyne and Thrush (70) reported the emission of a feeble red glow said to be arising from HNO during their spectroscopic study of the gaseous $H + NO$ reaction. However, Clement and Ramsay (69) reported that the radiation emitted from this reaction was not visible.

During the initial experimentation, the several reaction conditions were varied in an attempt to produce the red glow and/or the yellow explosive compound. The flow rates and pressures used by previous investigators (69,70,73) were duplicated. Also, in addition to reacting (or mixing) the gaseous nitric oxide with the discharged hydrogen, varying mixtures of hydrogen-argon and hydrogen-helium were passed through the discharge tube and subsequently mixed with the nitric oxide. None of the reaction conditions produced the red glow and at no time was a yellow compound condensed in the liquid nitrogen cooled reactor.

It should be mentioned that the yellow explosive compound described by Geib and Harteck could actually have been solid contaminated nitric oxide. A yellow compound could be condensed in the U-tube reactor if either the hydrogen or the nitric oxide were not carefully purified. The yellow compound was apparently an oxidation product of the nitric oxide, probably NO_2 . If pure or contaminated nitric oxide condensed at 77°K was allowed to rapidly warm (by removing the surrounding dewar of liquid nitrogen), the solid condensed film would crack and produce a click sound which could be taken to be an explosion. Considering these

observations, the yellow explosive compound described by Geib and Harteck was likely not HNO .

Results from the use of both the magnetic and the TOF spectrometers and associated inlet systems, as summarized in Table 1, indicate that only nitric oxide, nitrous oxide, and water were condensed from the reaction mixture. In attempting to detect nitroxyl, the hydrogen peak and also

Table 1. Products from the $\text{H} + \text{NO}$ Reaction

Temperature, $^{\circ}\text{C}$	Product Observed
-180	NO
-166	N_2O
- 90	H_2O

the part of the spectrum where the peak at $m/e = 31$ due to HNO would appear were constantly monitored during the controlled warm-up of the reaction product mass. Also, in the event that nitroxyl did not produce a parent positive ion (HNO^+), the peak at $m/e = 30$ was watched for any unusual increase in intensity. In no case was there any indication of the presence of stabilized nitroxyl. However, as will be seen shortly, these results were not too surprising.

Since the early work of Geib and Harteck, there have been three accounts of the trapping of HNO . Brown and Pimentel (67) and Robinson and McCarty (65) reported the stabilization of HNO in an argon matrix at 20°K and Harvey and Brown (73) condensed HNO in an argon matrix at 4°K . No experiments were described in which HNO had been stabilized without the use of a matrix or at a temperature as high as 77°K . In connection with this, Robinson (80) reported that his group had carried out warm-up

experiments on HNO stabilized in argon and in krypton matrices. He stated that HNO in argon began to disappear, presumably by reaction or dissociation, at about 25°K, and HNO in krypton began to disappear at about 36°K. From these observations, Robinson concluded that the quenching and stabilizing of HNO definitely required a rigid, inert matrix. This conclusion is consistent with the failure to observe HNO in the much higher temperature experiments of this thesis research.

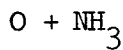
The experiments performed with the TOF mass spectrometer and cryogenic inlet system were significant in that the detection of nitrous oxide and water during the warm-up indicated that the short-lived nitroxyl molecule was probably present during the reaction process. Clyne (72) had previously reported that the HNO molecule was destroyed by the reactions



and



It is perhaps not too speculative to suggest that the vapor pressure of HNO would likely be somewhat less than that of NO. Solid NO exerts a vapor pressure of 0.1 mm Hg at 78°K while HNO is chemically lost at temperatures of 25° to 35°K. Hence, the likelihood of HNO existing as a chemical reagent at any temperature appears to be very unlikely.



The results obtained from the study of this reaction were significant in that a reaction product stable only at temperatures lower than

room temperature was detected. This identification was a direct indication that the cryogenic inlet system of the magnetic deflection spectrometer could be used in transferring unstable or semi-stable species from the reactor to the mass spectrometer without significant warm-up above the reactor temperature. Since the presence of this unstable compound, diimide, could be more firmly established from energy measurements, the reaction was also carried out in the TOF mass spectrometer cryogenic inlet system. The compounds produced by the atomic oxygen-ammonia reaction are listed in Table 2.

Table 2. Products from the $O + NH_3$ Reaction

Temperature Range, °C	Compounds Observed
-183 to -141	NO
-125 to -110	N_2H_2 , N_2 , N_2O , unreacted NH_3
- 61 to 1	H_2O
- 50 to - 15	N_2H_4
- 1 to > 1	NH_2OH
room temperature	NH_4NO_3

Nitric Oxide

Nitric oxide was identified in the range -183° to $-141^\circ C$ by its mass spectra and by measurement of its ionization potential, 9.4 ± 0.2 ev (81). When the atomic oxygen-ammonia reaction was carried out at room temperature with no low temperature quenching, nitric oxide and

nitrous oxide were the main reaction products. When the reaction vessel was slowly cooled below -115°C , the intensity of the peaks due to nitric oxide and nitrous oxide began to decrease, indicating that a portion of the species intermediate to the production of nitric oxide and nitrous oxide were being removed from the reaction zone by the low temperature quenching. It was obvious that the quenching was not completely effective since NO and N_2O were detected even when the quenching was carried out at 90°K . However, as shown in Table 2, a variety of intermediate compounds were formed as a result of the low temperature quenching.

Diimide

The mass of products condensed from the $\text{O} + \text{NH}_3$ reaction had a bright yellow color similar to that described by Geib and Harteck (1) in their earlier study of this same reaction. Geib and Harteck postulated that the yellow compound might be HNO or NH_3O . However, this work has shown that the yellow substance was actually the normally unstable compound, diimide. As indicated in Table 2 and in Figure 6, diimide, nitrogen, and nitrous oxide were detected in the temperature range -125° to -110°C with maximum evolution of each occurring at -115°C . It can be seen in Tables 7 and 8 in Appendix B that the maximum evolution of unreacted ammonia also occurred at about -115°C . On warming through the temperature range -125° to -110°C , the color of the deposit gradually changed from yellow to white, evidently as a result of pumping the diimide from the reactor. The observations just described agree well with previous observations on diimide summarized in Chapter 1. To reiterate, diimide can be condensed as a yellow solid at 90°K , it has a maximum evolution rate at about -113°C , a white deposit remains in the reactor

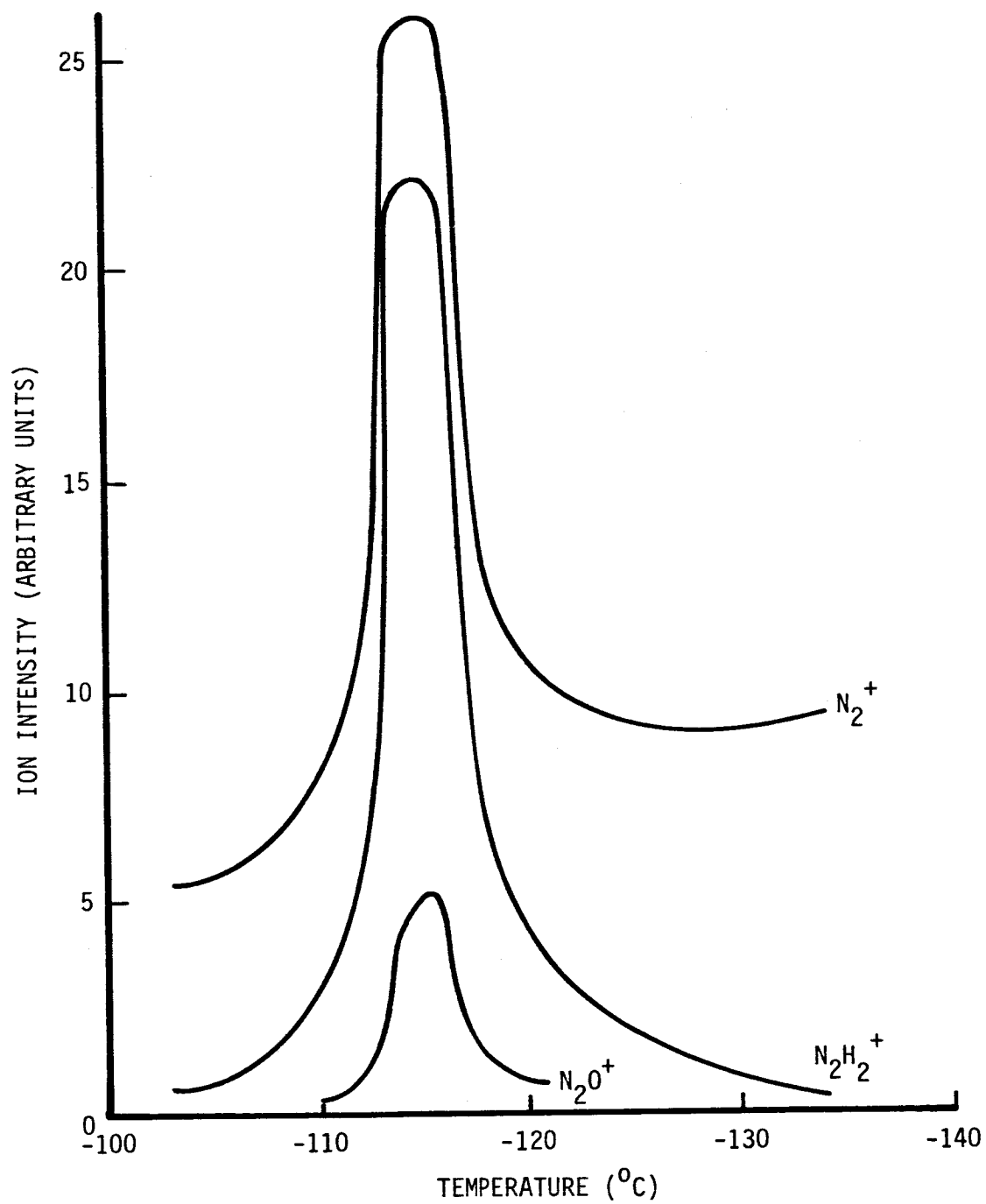


Figure 6. Variations of Ion Intensities with Temperature for Three Species from the $O + NH_3$ Reaction.

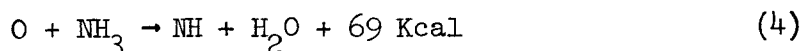
after the diimide vaporizes, and nitrogen evolves at the same time as diimide.

However, to further secure the identification of diimide, its ionization potential was measured in the TOF spectrometer. The ionization potential was measured at several relative ion intensities by the vanishing current method previously described by Smyth (82). This less accurate method was used due to the inability to obtain a sufficiently strong diimide signal to allow a semi-log matching type determination (83). Nitric oxide was used as the calibrating standard and its ionization potential was also measured at matching ion intensities by the same method. The results of these measurements are given in Figure 7 where the curve for diimide is seen to be constantly 0.4 ev higher than the curve for nitric oxide. Since the ionization potential of nitric oxide is 9.4 ± 0.2 ev, the ionization potential of diimide becomes 9.8 ± 0.2 ev. This is in agreement with the previously reported value of 9.85 ± 0.1 ev (14) and is final proof of the presence of diimide.

The diimide was probably formed by the combination of two NH radicals on the cold reactor wall according to the equation



As previously discussed, M is the third body (probably the cold reactor wall) which removes the excess energy of reaction. The NH radicals could have been formed by the reaction



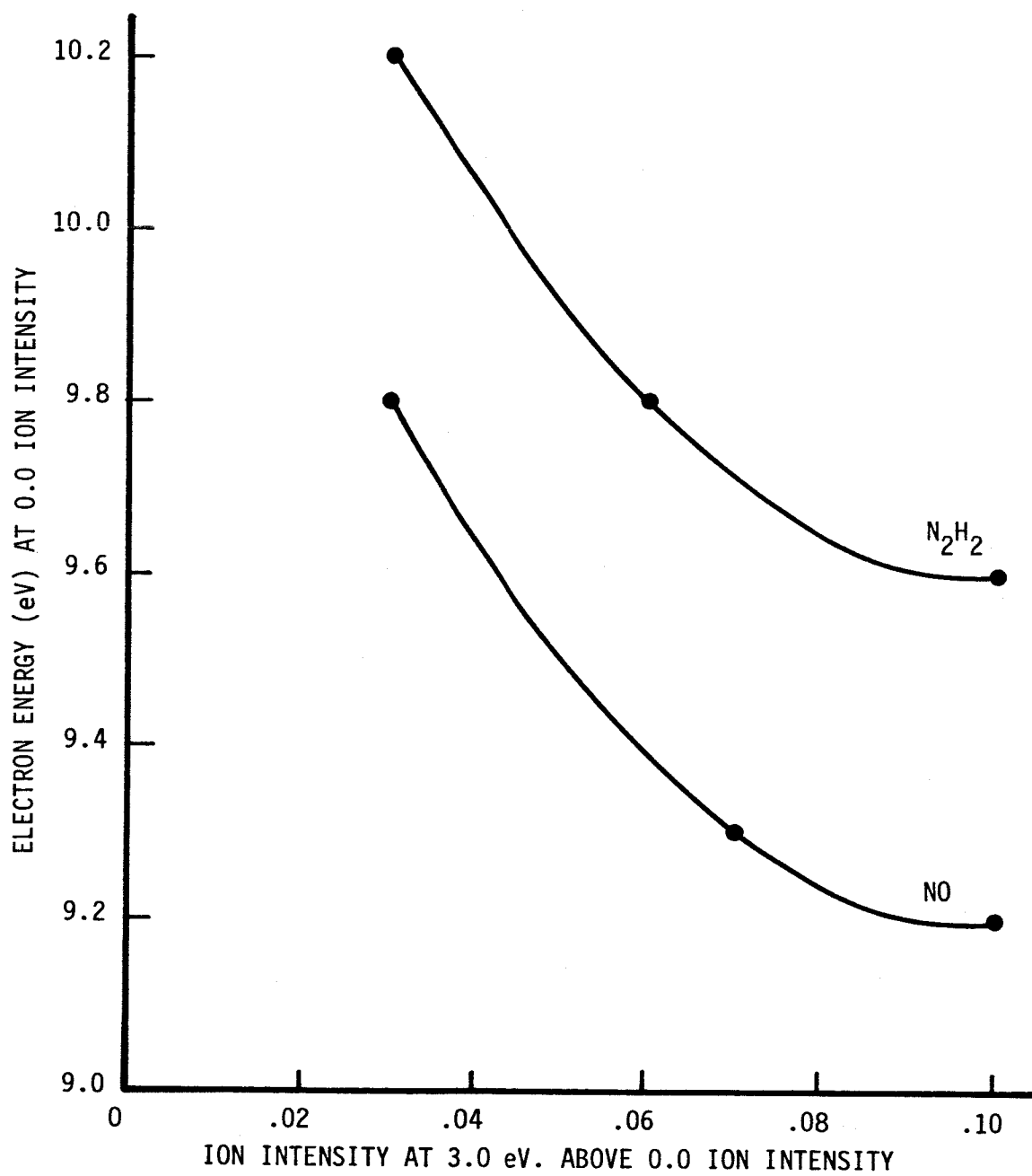
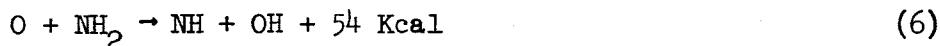
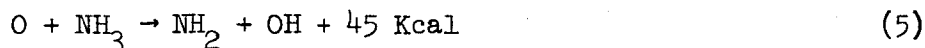


Figure 7. Ionization Potential Measurement of Diimide by Vanishing Current Method.

or by the reactions



all of which are obviously to be expected energetically. The heat of formation of NH (82 Kcal/mole) has been taken from a recent study by Reed and Snedden (84). In support of the proposed reactions, the NH_2 , NH, and OH radicals and water have previously been observed in ammonia-molecular oxygen flames (6,7).

Since the present work is the first account of diimide production by the $\text{O} + \text{NH}_3$ reaction, a number of interest would be the percent conversion. With the feed gas flow rates that were used, the percent conversion of ammonia to diimide was approximately 1.3 percent. This percentage was calculated from the relative ion intensities of the major peaks due to ammonia and diimide during their period of evolution from the reactor. It should be recognized that this ratio does not represent the exact percent conversion since the amount of diimide produced was compared to the amount of unreacted ammonia rather than to the amount of ammonia originally coming into the reactor. However, since the percentage of conversion was so small, the correction for the amount of reacted ammonia should be insignificant. In using the relative ion intensities, it was also assumed that the ionization cross sections for ammonia and diimide were equal. The ionization cross section of diimide is unknown, but it should not be different from that of ammonia by a factor of more than 1.5 (see table of typical ionization cross sections listed by

Reed (85)). Therefore, the percent conversion should be given as 1.3 ± 0.5 percent. The data used in this estimate of the percent conversion were taken from Table 7 in Appendix B.

Nitrous Oxide

This compound was identified by its mass spectra and by a measurement of its ionization potential, 13.1 ± 0.05 ev (86). The ionization potential was measured to be 13.3 ± 0.2 ev by the vanishing current method with the H_2O^+ ion as the calibrating standard.

Hydrazine

Hydrazine was identified in the range -50°C to -15°C by its mass cracking pattern (87)

<u>m/e</u>	<u>Ion</u>	<u>Intensity (%)</u>
32	N_2H_4^+	100
31	N_2H_3^+	47
29	N_2H^+	40
30	N_2H_2^+	31
16	NH_2^+	29

The variation of ion intensity ratios with temperature for the m/e peaks at 32 and 30 are shown in Figure 8. Only a small amount of hydrazine was present and the ion intensity ratios rather than intensity itself were used to smooth out the instabilities of the diffusion pump and the spectrometer control unit, thereby giving a better indication of the true ion intensity variations. The two curves in Figure 8 would have presumably exhibited minima at the same temperature if instabilities had not existed.

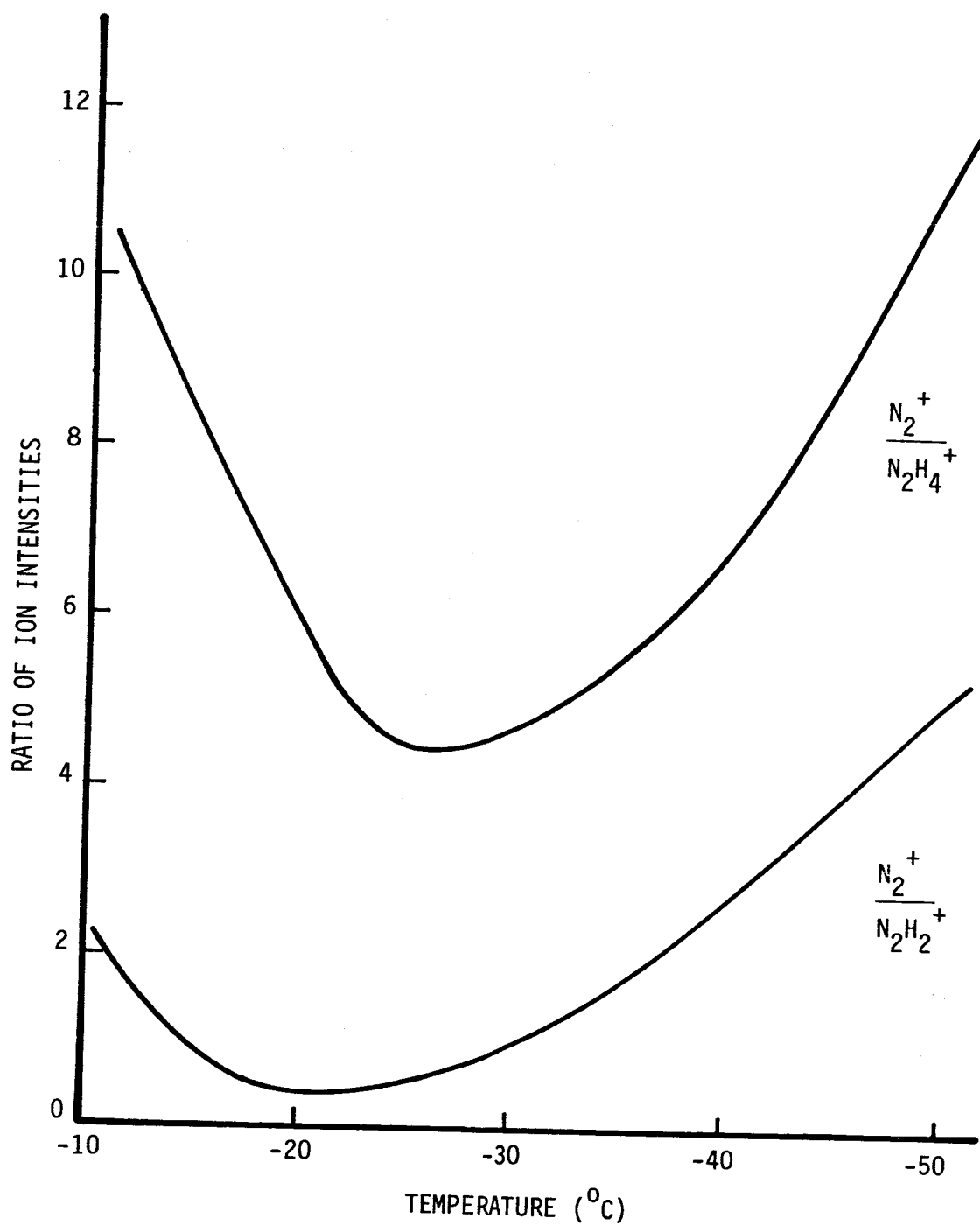
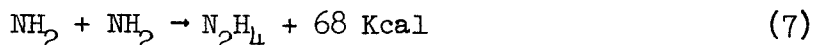


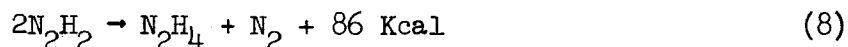
Figure 8. Variation of Ion Intensity Ratios with Temperature in the Detection of Hydrazine.

In further studies using the TOF mass spectrometer, the appearance potential of the N_2H_2^+ ion from hydrazine was found to be 11.3 ± 0.2 ev. This potential was determined by the semi-log matching method and can be compared to the previous values of 10.98 ± 0.02 ev and 11.9 ± 0.2 ev reported by Foner and Hudson (14) and Dibeler, Franklin, and Reese (19) respectively.

The hydrazine could have been formed by the combination of two NH_2 radicals



and also during the evolution and decomposition of part of the diimide according to the reaction



This last reaction would also explain the observed evolution of nitrogen at -115°C which always accompanied the diimide. The heat of formation of N_2H_2 (48.7 ± 5 Kcal/mole) was calculated by Foner and Hudson (14).

The atomic oxygen-ammonia reaction was the first reaction carried out using the cryogenic inlet system of Figure 3 and the connecting tubing was smaller than that used in the study of the other reactions. This smaller tubing resulted in a larger vapor pressure requirement for mass spectrometric detection. Accordingly, hydrazine appeared at -50°C where its vapor pressure was 4×10^{-2} mm Hg (88) and maximum evolution occurred at -24°C where its vapor pressure was 0.4 mm Hg. This compared favorably with the temperature of maximum evolution of ammonia, -115°C , where its

vapor pressure was also 0.4 mm Hg. With the larger vapor conduit that was used in all subsequent experiments, the minimum vapor pressure was reduced to 5×10^{-3} mm Hg and the pressure of maximum gas evolution was reduced to 0.1 mm Hg.

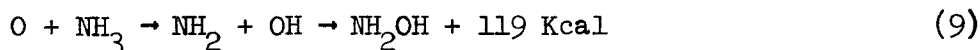
Hydroxylamine

The presence of hydroxylamine was confirmed by mass spectrometry and also from a qualitative chemical analysis. At -1°C , the intensity of the m/e peak at 33 (NH_2OH^+) began to increase. The vapor pressure of hydroxylamine was 0.04 mm Hg at this temperature and was therefore in the pressure range for detection as previously noted for hydrazine.

Prior to use of the mass spectrometer, the pressure of hydroxylamine was apparent from the addition of Fehling's solution to a water solution of the residue present in the reactor at 0°C . Since hydroxylamine is a reducing agent, its presence was noted when the Fehling's solution was reduced to form a yellow-red precipitate.

Hydrazine is also a reducing agent which produces the same colored precipitate when tested with Fehling's solution. However, as indicated in Figure 8, the hydrazine should have been pumped out of the reactor at temperatures lower than 0°C . In confirmation of this, an additional test solely for the presence of hydrazine (89) gave negative results.

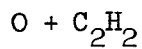
The detection of hydroxylamine was significant since it had previously been proposed to exist as an intermediate in the oxidation of ammonia (10). Hydroxylamine was probably formed by the reaction sequence,



or possibly by a direct insertion.

Ammonium Nitrate

The presence of ammonium nitrate was apparent from its physical appearance and from qualitative chemical analysis. At room temperature, a white solid remained in the reactor which could not be identified mass spectrometrically since it exhibited no apparent (at least 0.04 mm Hg) vapor pressure. Since ammonium nitrate is a white solid which melts at 169.6°C (78), qualitative wet chemical tests were made for the presence of the ammonium and the nitrate ions (90). Both tests were positive.



The reaction of oxygen atoms with acetylene occurred with the formation of a blue-green chemiluminescent flame. On being quenched to 90°K, the reaction flame yielded a yellow-red deposit of solid products. The product assignments and observations made during the controlled warm-up are summarized in Table 3.

Table 3. Products from the $\text{O} + \text{C}_2\text{H}_2$ Reaction

Temperature Range, °C	Compound Evolution	Observation
-163 to -135	Unreacted C_2H_2	
-163 to -135	CO_2	
-135 to -116	Secondary C_2H_2	red color fading
-103 to - 79	O_2	yellow color fading
- 82 to - 54	$(\text{CHO})_2$	yellow color fading
- 50 to - 20	HCOOH	
- 79 to - 20	H_2O	
room temperature		white, fluffy solid



It was found experimentally that an excess of acetylene was required to sustain the bright reaction flame and produce the colored reaction products. During the warm-up, an evolution of acetylene occurred in two different temperature ranges. This is shown in Figure 9 which is a plot of the intensity variation of the C_2H^+ ion from acetylene during the warm-up. During the secondary evolution of acetylene (-135° to -115°C), the red color began to fade and finally disappeared near -115°C . The secondary evolution did not occur when a blank sample of unreacted acetylene was condensed and warmed, and it was then evident that the red color and the secondary acetylene evolution were related.

One possible way to account for the acetylene evolution-red color relationship would be in terms of a charge transfer complex. The complex might be formed by the association of π electrons of acetylene with the proton from formic acid. This is indicated in Figure 10 where two pictures of the charge transfer (or electron association) complex are presented. In Figure 10(a), the arrow denotes that electrons of the acetylene triple bond are associated with the proton from formic acid. In Figure 10(b), the formic acid proton is shown interacting with the π electrons of the acetylene triple bond.

The red color of the complex would be caused by the transfer of electrons from the acetylene to the formic acid. This electron transfer would be to a lower excited state and cause a shift toward longer wavelengths of absorption. This type of absorption shift is well known. For example, when chloranil (yellow) and hexamethylbenzene (colorless) are mixed together, an intensely red solution is formed (91). The red

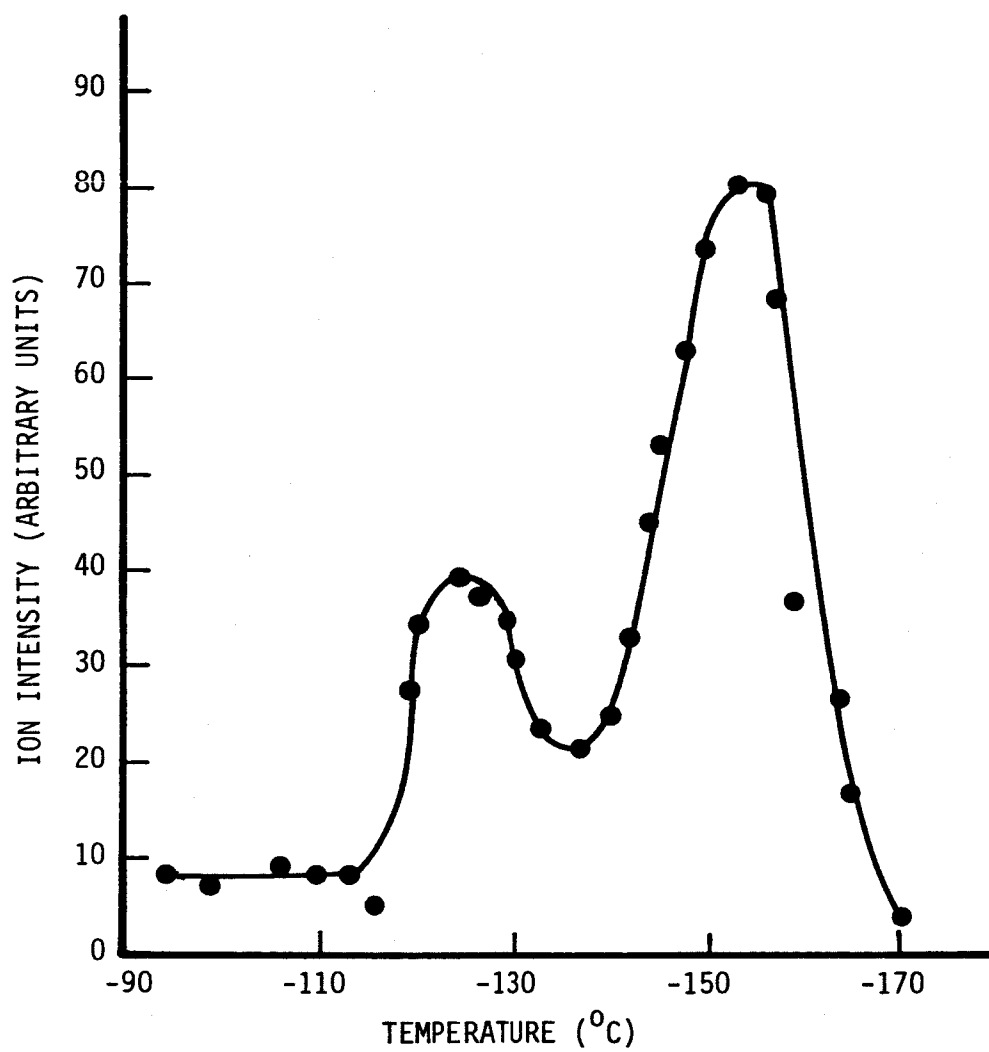


Figure 9. Intensity Variation with Temperature for C_2H^+ Ion from Acetylene.

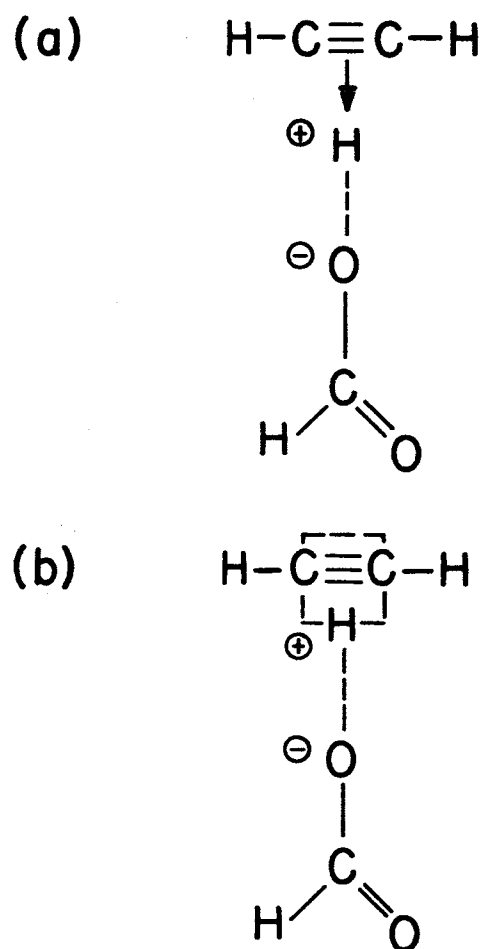


Figure 10. Two Representations of Charge Transfer Complex of Acetylene and Formic Acid.

color is due to light absorption by a charge transfer complex of the two compounds. In the present proposal, the acetylene and formic acid would exist only as a low temperature charge transfer complex. On warming, the association would decrease and result in the evolution of acetylene.

In defense of the charge transfer complex proposal, benzene will also react with oxygen atoms to form red deposits at 90°K , as was determined as part of this thesis research. No reaction product analysis was made, however, charge transfer complexes of benzene are well known (92) and the red deposit could be another example of such a low temperature complex.

O_2 , $(\text{CHO})_2$

As indicated in Table 3, both oxygen and glyoxal evolved from the reactor during the fading of the yellow color. Since glyoxal exists as a yellow solid melting at 15°C (78), the fading color is apparently a result of the pumping of the glyoxal from the reactor.

Only a slight amount of oxygen evolved from the reactor (see Table 10 in Appendix B) and its origin and significance were not established.

Room Temperature Solid

A white, fluffy solid reaction product remained in the reactor after warming to room temperature. On exposure to the atmosphere, the color of the solid gradually became yellow, and after approximately 48 hours, the color finally changed to a dark red-brown. The yellow solid resembled hard, amorphous sulfur and the dark red-brown solid appeared as a thick, resinous material. Both the yellow and brown solids were soluble in acetone, slightly soluble in water, and insoluble in carbon

disulfide and carbon tetrachloride.

The infrared spectra of the yellow and brown solids were obtained to enable some statements to be made about the type of compounds present. From the summary of wavelength assignments given in Table 4, both unsaturated ester ($=\text{CH-CO-O-R}$) and aldehyde (CHO) groups appeared to be present. In addition, OH groups were present which were likely involved in intermolecular polymeric association. When the infrared spectrum of

Table 4. Wavelength Assignments for Yellow Solid
Produced by the $\text{O} + \text{C}_2\text{H}_2$ Reaction

Wavelength, microns	Interpretation
2.95	intermolecularly hydrogen bonded OH (polymeric association)
3.4	CH
5.80	ester group, unsaturated $=\text{CH-CO-O-R}$
6.05	aliphatic aldehyde group, unsaturated $\text{C} = \text{O}$
6.4	---
7.2	characteristic of aliphatic aldehydes
8.5 - 9.0	ester fingerprint region
9.0 - 10.5	aldehyde fingerprint region

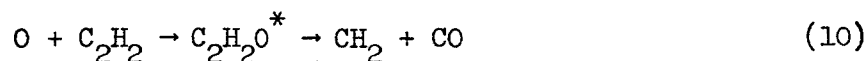
Characteristic frequencies taken from Absorption Spectroscopy of Organic Compounds (93).

the brown solid was obtained, there were four apparent changes from the spectrum obtained with the yellow solid. The intensity of the aldehyde peaks at 6.05 and 7.2 microns increased as did the intensity of the broad aldehyde band near 9.25 microns, apparently at the expense of a reduction in intensity of the band in the ester fingerprint region. In

the absence of additional information, no attempt will be made to draw a hypothetical compound structure. However, the color and infrared spectra changes seemed to indicate that reactions of oxidation, hydrolysis, and/or decomposition were occurring to increase the concentration of aldehyde groups. The color changes could be explained by an increase in the number of C = O groups or by an increase in system conjugation.

General Reaction Mechanism

Fenimore and Jones (29) first proposed that the reaction of oxygen atoms with acetylene would proceed with the initial formation of an unstable energy-rich compound according to

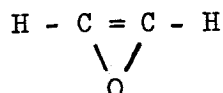


One result in support of this proposal is that of Haller and Pimentel (30) who reacted ^3P oxygen atoms and acetylene at 20°K in a solid argon matrix and reported the formation of ketene.

The failure to detect ketene in the present work seemed to indicate that the quenching process was not fast enough to stabilize that energy-rich molecule. When compared with the $\text{O} + \text{C}_2\text{H}_4$ reaction in which the initial reaction product, ethylene oxide, has three more bonds than ketene to absorb the energy of reaction, it is apparent that this could possibly be the reason for the difference in stabilization efficiency.

One other point which should be considered is the relative effects of reaction with triplet and singlet oxygen atoms. Haller and Pimentel (30) reacted ^3P oxygen atoms with acetylene to form ketene by a process similar to that described by Cvetanović for the $\text{O} + \text{C}_2\text{H}_4$ reaction (see discussion in Chapter I). If ^1D oxygen atoms were reacted with acetylene,

the electron spins would be lined up such that addition would occur across the carbon atoms, and the initial reaction product would likely have the structure of an oxirene:



Since ^1D oxygen atoms are more energetic than ^3P oxygen atoms by 45 Kcal/gm-atom, the reaction with ^1D atoms would be more exothermic. Also, the oxirene would be more unstable than ketene because of the highly strained ring structure. Not surprisingly, this species was not observed even though, as discussed in Chapter II, ^1D oxygen atoms should be present in the reaction zone.

The formation of the several other identified reaction products can be explained in a manner similar to that for the $\text{O} + \text{C}_2\text{H}_4$ reaction. The ketene and oxirene would decompose according to



or

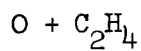


The radicals would further react with the oxygen atoms or molecules or might dimerize to form glyoxal, ethylene, etc.

Analytical Limitations

The limitations of the mass spectrometer were apparent in the preceding descriptions of reaction product identifications. The red compound could not be directly identified, the origin of the oxygen evolution could

not be established, and since the room temperature solid exerted no apparent vapor pressure, other analytical methods had to be used. The significance of the limitations depends on the purpose of the research. If the main purpose is to identify all of the reaction products, the limitations are serious. However, the limitations are less serious if one is more interested in the synthesis of low temperature compounds in quantities and in purities such that they may be considered to be chemical reagents.



The products obtained from this reaction are listed in Table 5.

Table 5. Products from the $\text{O} + \text{C}_2\text{H}_4$ Reaction

Temperature Range, °C	Product Observed
-176 to -152	unreacted C_2H_4
-163 to -131	CO_2
-145 to -121	HCHO
-127 to -94	CH_3CHO , CH_2OCH_2
-82 to -54	CH_3OH
-65 to -10	H_2O
-60 to -10	HCOOH

Since all of the compounds were well known, they were identified by their mass cracking patterns and by use of the characteristic of the apparatus that maximum evolution occurred at the temperature when each compound exerted a pressure of approximately 0.1 mm Hg. Carbon monoxide was most

likely formed during the reaction (see products reported by Cvetanović (49) and by Avramenko and Kolesnikova (47)); however, since it would not condense in the reactor at 90°K, it was not detected. The temperature-vapor pressure data used in the identifications are tabulated in Table 6 in Appendix A. All of the compounds listed in Table 5 are stable at normal temperatures, and it was initially thought that the results obtained from the $O + C_2H_4$ reaction were not very significant. However, after a comparison with other studies of the oxygen atom-ethylene reaction carried out under more ordinary conditions, some interesting conclusions were drawn and are discussed below.

No attempt was made to determine the relative amounts of each product, however, it can be seen in Table 11 in Appendix B that the largest pressure increase occurred during the evolution of the acetaldehyde-ethylene oxide mixture. The vapor pressures of acetaldehyde and ethylene oxide were so similar that no separation of the two compounds occurred during their evolution from the reactor. The ratio of acetaldehyde to ethylene oxide was estimated to be 28:72 by assuming approximately equivalent ionization cross sections. For acetaldehyde, the ratio of the peak at $m/e = 43$ to the peak at $m/e = 44$ (43/44) was 0.78, and for ethylene oxide, the 43/44 ratio was 0.24. These ratios were taken from the American Petroleum Institute tables (87) and were confirmed by injecting samples of acetaldehyde and ethylene oxide into the spectrometer system used in this thesis research.

This detection of large amounts of ethylene oxide was in direct contrast with earlier results of Cvetanović (49) and of Avramenko and Kolesnikova (47). Cvetanović reacted oxygen atoms and ethylene and re-

ported that only a trace of ethylene oxide was detected in the reaction products. Studying the same reaction, Avramenko and Kolesnikova did not report the formation of any ethylene oxide.

These different observations may be reconciled by a consideration of the reaction conditions. Both Cvetanović and Avramenko and Kolesnikova carried the reactions out at or above room temperature. In strong contrast, in the present work the reaction products were immediately quenched to 90°K. The fast, low temperature quenching evidently stabilized much of the ethylene oxide, thereby reducing the amount of subsequent rearrangement to acetaldehyde or decomposition and further reaction.

The low temperature stabilization of ethylene oxide lent support to the $O + C_2H_4$ reaction mechanism proposed by Cvetanović. As discussed in Chapter I, Cvetanović suggested that the initial reaction product was an energy-rich ethylene oxide molecule which decomposed to form the final products. Cvetanović based his proposal on the appearance of small amounts of ethylene oxide and on the types of final products which were formed in his experiments. As noted above, the present detection of large amounts of ethylene oxide form a stronger basis for his proposal.

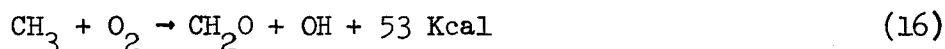
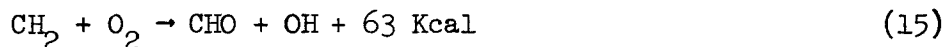
The low temperature isolation and stabilization of ethylene oxide was similar to that of diimide. Both molecules were formed by exothermic reaction and their decomposition was partially halted by the low temperature removal of the energy of reaction. The most significant difference was that diimide was unstable at room temperature.

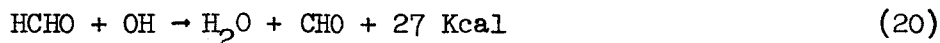
A further comparison of the reaction products reported in the present work with those reported by Cvetanović yielded more interesting information. Cvetanović initially carried out the $O + C_2H_4$ reaction in

a system completely free of molecular oxygen. When molecular oxygen was added, large quantities of formaldehyde, formic acid, alcohols, and water were formed. In the absence of molecular oxygen, none of these species appeared as products. Cvetanović attributed their formation to the free radical scavenger action of the molecular oxygen. The same products were detected during the present reaction study, and as just noted, this was a strong indicator of the presence of molecular oxygen. This is not surprising since the distance from the discharge tube to the reactor was approximately four feet and a considerable amount of atom recombination was expected. The present study could be more correctly designated as $O + O_2 + C_2H_4$.

The large number of reaction products listed in Table 5 is a direct indication that, as in the case of the $O + NH_3$ reaction, the low temperature quenching did not completely arrest the reaction to the point of preventing the formation of the final products that have been observed in studies at more ordinary conditions. In the $O + C_2H_4$ reaction, the final products would be CO_2 and H_2O .

The CO_2 , $HCHO$, CH_3OH , H_2O , and $HCOOH$ were probably formed as a result of several decomposition and radical reaction processes. Some of the possible reactions are





The asterisk represents the presence of excess energy.

Since the U-tube reactor was made of pyrex and was cooled by the use of clear refrigerants, visual observation of the products during reaction and also during the warm-up process was possible. When the $\text{O} + \text{C}_2\text{H}_4$ reaction was carried out, the quenched reaction deposit was yellow. On warming to -110°C , the yellow deposit melted to form a viscous, clear, yellow tinted liquid. This liquid was pumped away leaving behind in the reactor a white solid at -102°C . During further warming a clear film accompanying the white solid was noted at -80°C . The clear film was probably present at lower temperatures, however, it was not noticed until small bubbles began to form at -80°C .

After matching these observations with the corresponding mass spectral data, the following model may be suggested. The yellow tinted liquid was a low temperature solution of acetaldehyde, ethylene oxide, methanol, water, and formic acid. The acetaldehyde and ethylene oxide were pumped away leaving the white deposit of methanol, water, and formic acid at -102°C . The clear liquid noted at -80°C was methanol (melting point -97°C). The origin of the yellow color was not established, however, it could have been caused by some low temperature molecular interaction or by a small amount of some unidentified impurity.

Upon continued study of the reaction at lower flow rates such that

all of the ethylene was reacted before it deposited, the entire mass of reaction products condensed to form a yellow tinted glassy appearing solid. On warm-up, carbon dioxide, formaldehyde, and the above mentioned compounds evolved from the yellow-glassy reaction mass. In other experiments with higher ratios of ethylene to oxygen, it was realized that the yellow solid deposit was evidently a mixture of the yellow glass and the unreacted ethylene. The unreacted ethylene formed a white background for the yellow-glassy product mass.

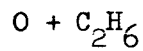
The appearance of the yellow glass was an unusual result since all of the compounds will condense separately as white solids at 90°K . As mentioned above, the appearance of the yellow glass was explained in terms of a solid solution which changed to a liquid solution on warming to -110°C . Since the liquid solution disappeared at -102°C when the acetaldehyde and ethylene oxide were pumped away, this seemed to indicate that acetaldehyde and ethylene oxide were the low temperature solvents.

A lower limit on the concentration of oxygen atoms present in the reaction zone was calculated from the flow rates used during the complete reaction of ethylene. In the comments section of Table 12 in Appendix B, it can be seen that the He-O_2 flow was $24.0 \text{ std.cm}^3/\text{min}$ when the lowest C_2H_4 flow was $0.85 \text{ std.cm}^3/\text{min}$. Assuming that the oxygen atoms were consumed only by the reaction



it was calculated that the discharged gas entering the reactor contained at least 4 percent oxygen atoms.

As a matter of interest, it was calculated that, at a He-O₂ flow rate of 24.0 std. cm³/min and 1.3 mm Hg pressure, it would require 0.3 seconds for a molecule (or atom) to travel from the discharge tube to the reaction zone of the U-tube reactor.



In contrast with the reaction of oxygen atoms with ammonia, ethylene, and acetylene, the reaction of oxygen atoms with ethane produced only one product. As indicated in Table 4 in Appendix B, ethanol was detected in the range -60° to -37°C with a maximum rate of evolution at -51°C at which point it exerts a vapor pressure of 0.15 mm Hg. Also indicated in Table 14 is the presence of ozone and nitrogen dioxide. Ozone and nitrogen dioxide are not termed reaction products since they contain no carbon or hydrogen atoms. This unusual combination of compounds was observed in studies of this reaction using both the TOF and the magnetic spectrometers and associated cryogenic inlet systems.

In addition to the differences in the relative number of reaction products, the oxygen reaction with ethane was also marked by a slow rate of reaction. This general result was expected since the relative reactivities of saturated and unsaturated hydrocarbons are well known (94).

Previous studies of the oxygen atom-ethane reaction at or above room temperature have resulted in the detection of carbon dioxide, carbon monoxide, ethanol, formaldehyde, acetaldehyde, and water as reaction products (54,55,56,57). After comparing the reaction conditions and products of the previous studies with that of the present work, some interesting conclusions can be drawn. The most obvious comparison is the

greatly altered number of reaction products. Evidently the rapid low temperature quenching has eliminated fragmentation of the initial reaction product (ethanol) and has also prevented the occurrence of secondary reactions. This reaction is an example of a successful attempt to isolate and stabilize the initial reaction product. As discussed in the Introduction, this method of low temperature quenching can give evidence as to the steps involved in the reaction mechanism. Accordingly, it can be concluded that ethanol is the primary reaction product, and the products detected by the earlier investigators occur as a result of fragmentation and further reaction of ethanol with the incoming oxygen atoms and molecules.

Since ethanol alone has been detected, it seems likely that it is formed by an insertion type reaction with the oxygen atoms. As discussed in Chapter II, both ground state triplet oxygen atoms (O^3P) and excited state singlet oxygen atoms (O^1D) are to be expected as a result of the highly energetic electric discharge. Because of the different spin multiplicities, the triplet and singlet oxygen atoms should exhibit differences in chemical behavior in interactions with ethane. The triplet oxygen atom has two electrons of parallel spin and would be expected to abstract a hydrogen atom from the ethane. The excited singlet oxygen atom has two electrons of opposite spin and these electrons would line up with the electrons of opposite spin in the C-H bond to form ethanol as the insertion product. These electron interactions are shown in Figure 11. The triplet oxygen attack should produce several reaction products since both the C_2H_5 and OH radicals would be present for further reactions among themselves and with atomic and molecular oxygen. The

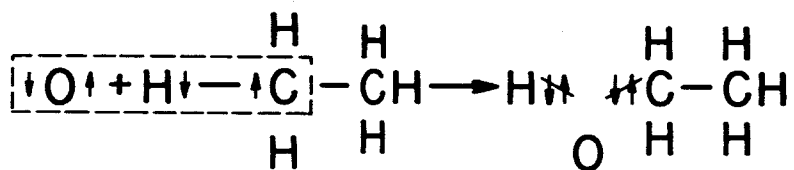
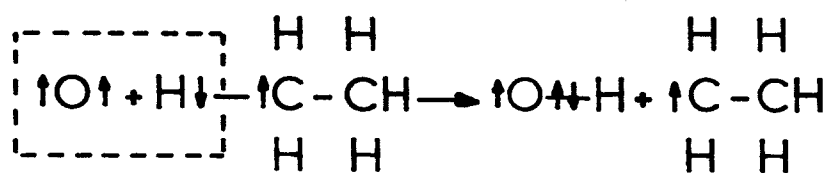


Figure 11. Expected Interactions of Triplet and Singlet Oxygen Atoms with Ethane.

singlet oxygen atom attack should initially produce an energetic molecule of ethanol which could then (1) be stabilized by collisional deactivation or low temperature quenching, or (2) fragment to form simpler radicals which could continue to react in a complex manner, or (3) undergo further oxidation reactions. From these considerations, the dominant reaction is apparently that of singlet oxygen atoms with ethane, and the resulting ethanol is stabilized by the low temperature quench. The absence of products from the reaction of triplet oxygen atoms might be explained by the greater reactivity of the excited atoms and the formation of small amounts of products below the detection limit of the spectrometer.

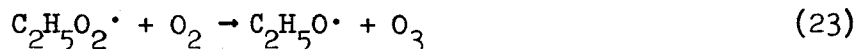
These conclusions are supported by previous related work. Wright (57) reacted triplet oxygen atoms with ethane and reported the main reaction products to be formaldehyde, acetaldehyde, and water. Yamazaki and Cvetanović (58) selectively reacted triplet and singlet oxygen atoms with propane and reported that alcohols were formed as a result of reaction with singlet atoms, and abstraction products (2-methyl pentane, n-hexane) were formed as a result of reaction with triplet atoms.

It was mentioned in Chapter I that the so-called peroxide and the aldehyde theories had been proposed to explain the mechanism of hydrocarbon oxidation. Since the present low temperature study did not result in the detection of any unstable hydroperoxides (CH_3OOH or $\text{C}_2\text{H}_5\text{OOH}$), it was at first speculated that this might have a bearing on the peroxide theory of oxidation. However, since the aldehydes were also absent, it appeared that the reaction was not proceeding by either of the proposed mechanisms. The initial step in both of these molecular oxidation mechanisms is the formation of an alkyl radical, and the presence of ethanol

without any accompanying products indicates that the reactions of singlet atomic oxygen and molecular oxygen are dissimilar processes. Therefore, no contribution was made to either of the proposed mechanistic theories.

The presence of nitrogen dioxide and ozone was also noted in the quenched reaction mass. The nitrogen dioxide was probably formed as a result of a small air leak in the ethane valving connections to the reactor. No nitrogen dioxide was present in either of the feed gases, He-O₂ and C₂H₆, and no nitrogen dioxide was formed during any of the other oxygen atom reactions.

Following a suggestion by Schubert and Pease (95), the presence of ozone was tentatively explained by the reaction



However, this possibility was rejected when it was realized that the sole presence of ethanol indicated the absence of alkyl and alkoxy radicals.

A more likely proposal for the formation of ozone has been developed, but before it is presented, some additional experimental observations should be mentioned. First, the ozone only appeared during quenching of the ethane reaction at 90°K and did not occur during any other oxygen atom reaction. Second, with the experimental apparatus used, ozone could not be quenched at 90°K when only discharged helium-oxygen was pumped through the reactor.

Since the reaction of oxygen atoms with ethane was the slowest reaction studied, there should have been a greater number of oxygen atoms present to react according to



where M is the third body necessary to remove the excess energy of reaction. In the other faster reactions, most of the oxygen atoms would be removed by reaction with the second reactant (ammonia, acetylene, or ethylene). In the presence of the continuous deposition of ethanol and unreacted ethane, the rate of evaporation of the ozone should be decreased. As contrasted with the situation where no ozone was condensed in the "clean" reactor, the ethane and ethanol deposition would make it more difficult for the ozone to be pumped upward away from the cold walls. It is possible to also imagine that the ethane and ethanol could dissolve ozone and hence decrease the rate of ozone evaporation by the formation of either a solid or a liquid solution. Either or both of these phenomena could account for the accumulation of liquid ozone.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1) The electrodeless electrical discharge arrangement developed herein can be used to transfer the maximum possible amount of power from the radio frequency power supply to the plasma, thereby maximizing the production of atomic species.

2) The reaction system can be used to carry out atomic hydrogen or atomic oxygen reactions with a second compound in a reactor located a distance of at least 4 feet from the discharge tube.

3) The fast low temperature quenching produced by the cold reactor walls can stabilize initially energy-rich reaction products and can also lead to synthesis of compounds which are unstable at room temperature. The extent of the low temperature stabilization depends greatly on the relative molecular complexity, energy content and reactivity of each reaction product.

4) The liquid refrigerant system can be easily and safely used in controlling the temperature of the reactor and cryogenic inlet system. The maximum temperature gradient present in the inlet system (at 77°K) was 3.5°K.

5) The cryogenic inlet system to the magnetic deflection mass spectrometer can be used for the detection of compounds if they exert a stable vapor pressure of at least 5×10^{-3} mm Hg in the temperature range

77° to 300°K. Maximum product evolution from the reactor occurs at the temperature where the product exerts a vapor pressure of 0.1 ± 0.05 mm Hg.

6) The mass cracking patterns produced by the small MS-10 mass spectrometer are similar to the cracking patterns reported in the API tables (87) and can be used in identifying the gases evolving from the reactor.

7) The reaction of hydrogen atoms with nitric oxide followed by a rapid quench to 77°K produced only small amounts of nitrous oxide and water. Although no HNO was detected, the presence of nitrous oxide and water indicated that HNO was present during the reaction process (72). The failure to stabilize and detect HNO is in agreement with recent results of Robinson (80).

8) The reaction of oxygen atoms with ethane followed by a rapid quench to 90°K produced ethanol as the only reaction product. This was an example of a successful attempt to stabilize the initial reaction product by low temperature quenching. The reaction probably occurred by an insertion of ^1D oxygen atoms into the carbon-hydrogen bond.

9) The reaction of oxygen atoms with ammonia at room temperature produced nitric oxide as the main reaction product. When quenched to 90°K, the conversion to nitric oxide was reduced and several intermediate products were formed. The products were nitrous oxide, diimide, hydrazine, hydroxylamine, water, and ammonium nitrate. The ionization potential of diimide was measured to be 9.8 ± 0.2 eV in agreement with an earlier value (14). The identification of diimide demonstrated the capability of the cryogenic inlet system to detect species stable only below room temperature. The detection of nitric oxide in the product

mass, when the reaction was quenched to 90°K , indicated that the low temperature quenching was not fast enough to completely prevent formation of the final products observed without quenching.

10) The reaction of oxygen atoms with ethylene followed by a rapid quench to 90°K produced carbon dioxide, formaldehyde, acetaldehyde, ethylene oxide, methanol, water, and formic acid. The detection of the relatively large amount of ethylene oxide supported a proposal by Cvetanović that the initial reaction product was an energy-rich ethylene oxide molecule. The large amount of ethylene oxide produced in the present work was a direct result of low temperature quenching. The presence of the formaldehyde, methanol, and formic acid suggested that molecular oxygen also entered into processes occurring in the cooled reactor.

11) The reaction of atomic oxygen with acetylene followed by a rapid quench to 90°K produced carbon dioxide, glyoxal, formic acid, water, a red compound or complex disappearing at -123°C , and a white solid which slowly changed to a yellow and finally to a brown color on exposure to the atmosphere at room temperature. The red substance was tentatively explained in terms of a charge transfer complex between unreacted acetylene and formic acid. The room temperature solid was not identified but was found to contain functional groups of aldehydes and esters. The expected initial reaction product, ketene, was not detected.

Recommendations

1) The reactions should be repeated under more controlled conditions by using oxygen atoms in the absence of molecular oxygen.

2) The product variation caused by the reaction of ^3P or ^1D oxygen atoms should be investigated.

3) The sensitivity of the mass spectrometer could be improved by using a shorter length, larger diameter capillary.

4) A miniature high vacuum valve capable of operation at 77°K should be placed in the line between the reactor and cryogenic inlet system. This would act as a controllable throttle and would permit continuous sampling of the gases evolving from the reactor during reaction.

5) The purification of diimide by low temperature rectification should be attempted. Reactions of diimide with simple organic compounds should be investigated.

6) The red compound produced in the $\text{O} + \text{C}_2\text{H}_2$ reaction should be studied by the use of low temperature optical spectroscopy or nuclear magnetic resonance spectrometry.

7) The solid compound produced in the $\text{O} + \text{C}_2\text{H}_2$ reaction should be identified. One possible method of identification would be to use a heated sample inlet tube to the mass spectrometer. The source structure of the mass spectrometer should also be heated to prevent excessive deposition.

8) Lower temperatures and/or solution reactions should be used in attempting to stabilize the initial product from the $\text{O} + \text{C}_2\text{H}_2$ reaction.

APPENDIX A

REACTION PRODUCT VAPOR PRESSURE DATA

The vapor pressure data used in this thesis research are listed in Table 6. The temperatures at which the products exerted vapor pressures of 0.1 mm Hg were extrapolated from plots of $\ln P(\text{mm Hg})$ versus $1/T(^{\circ}\text{K})$. The majority of the plotted data were taken from a compilation by Stull (77) listed in a standard reference source (78). The vapor pressures of glyoxal and ketene were calculated using methods recommended by Reid and Sherwood (96).

Table 6. Temperature-Vapor Pressure Data Used In Identification of Reaction Products

Compound	Temperature at 0.1 mm Hg Vapor Pressure, °C
NO	-195
N ₂ O	-155
H ₂ O	- 40
N ₂ H ₄	- 40
NH ₂ OH	+ 9
NH ₃	-123
C ₂ H ₂	-155
CO ₂	-147
CH ₂ CO	-140
CH ₃ OH	- 67
HCOOH	- 45
(CHO) ₂	- 77
CH ₂ OCH ₂	-109
CH ₃ CHO	-100
C ₂ H ₅ OH	- 55
C ₂ H ₄	-182
C ₂ H ₆	-172
O ₃	-192

APPENDIX B

BASIC EXPERIMENTAL DATA FOR OXYGEN ATOM REACTIONS

The main type of data obtained using the combination reactor system, cryogenic inlet system, and magnetic deflection mass spectrometer, was the variation of ion intensities with temperature during the controlled warm-up from the quenching temperature. The data were used in making the reaction product identifications and in evaluating the operation of the mass spectrometer and inlet system.

The basic raw data for the oxygen atom reactions are presented in the following tables. The reaction conditions and product identifications are listed at the bottom of each table. A small + sign in these tables indicates that the ion intensity was off scale in spite of the spectrometer having a dynamic range of 10^5 . The recorded pressures were measured with a thermocouple gauge and therefore must be considered only as rough indicators.

Table 7. Data from $O + NH_3$ Reaction, -135° to $-110^\circ C$

ION CURRENTS (Arbitrary Units)

Temp. $^\circ C$	-135	-130	-126	-124	-121	-120	-119	-118	-116	-115	-113	-110
Press. μ	10	20	37	54	82	96	122	205	143	128		100
m/e												
12	6.2	6.4	5.6	5.4	5.8	6.6	7.4	15	10	10	11	8.8
13	1.7											3.4
14	31.0	43	50	66	120	175	210	260	260	240	240	200
15	12.5	25	43	65	120	175	280	460	550	560	540	490
16	37	115	205	330	600	800	+	+	+	+	+	+
17	42	98	170	260	480	640	+	+	+	+	+	+
18	62	67	63	57	56	48	45	48	55	56	57	54
24												
25												
26												
27	5.3	4.7							4.6	4.4		3.2
28	9.4	9.0	9.4	10.0	11.7	17	20	25	15.5	11	10	6.2
29	10	8.6	8.0	7.2	6.3	5.7	4.8	5.8	6.1	5.8	5.7	4.6
30	.44	1.2	2.3	3.4	6.0	11.5	16	21	11.0	6.0	3.2	1.2
31	.20	.32	.33	.30	.37	.40	.22	.24	.14	.06	.06	.08
32	.68	.68	.72	.70	.50	.50	.30	.48	.46	.40	.40	.36
33												
39	1.5	1.3	1.2				.64					.74
40												
41	4.8	3.7	3.8	3.4	2.8	2.2	2.2		4.0	3.2	2.8	2.0
42												
43	2.0	1.6	1.5	1.3	1.1	1.1	1.1		1.9	1.5	1.1	.9
44				.60	1.3	1.5	2.8	4.4	1.8	.70	.36	
45		.38	.34	.34	.50	.50	.32					
46												
47												
48												
49												
50												
58	1.0	1.8	2.2			1.1	2.7		3.4		2.4	1.3

COMMENTS

Quenching temperature $-183^\circ C$ (liquid oxygen)

Reaction pressure 1 mm Hg

Helium-Oxygen flow 12.9 std. cm^3/min .Ammonia flow 7 std. cm^3/min .

Propane used as refrigerant during warm-up

Maximum evolution of ammonia at $-115^\circ C$ Maximum evolution of nitrogen, nitrous oxide, and diimide at $-118^\circ C$

Table 8. Data from O + NH₃ Reaction, -119°C to +2°C

ION CURRENTS (Arbitrary Units)

Temp. °C	-119	-116	-113	-110	-108	-106	-102	- 99	- 85	- 82	- 77	- 71
Press. μ	150	195	205	108	93	135	140	100	15	22	25	34
m/e												
12	15	20	17	10.4	9.2	8.8	7.8	7.0	6.7	5.1	4.9	5.9
13	3.2	6.8	5.0	3.11	2.5	2.7	2.4	2.1	2.0	1.5	1.4	1.9
14	300	620	540	170	120	170	155	155	37	51	49	54
15	200	360	570	330	235	320	290	330	66	95	88	100
16	1000	+	+	+	1000	+	+	+	175	430	290	350
17	+	+	+	+	1000	+	+	+	150	330	250	200
18	120	180	180	98	53	59	52	55	12	24	17	14
24												
25	.82	2.2	1.9						.17			
26	6.1	13	8.2	3.2	2.3	2.3	2.2	2.2	1.35	1.2	1.25	1.8
27	28	31	25	10.5	6.5	8.2	7.5	8.0	4.4	4.0	4.0	5.3
28	170	300	155	20	8.7	20	16.5	17	3.3	3.6	3.1	3.5
29	49	48	37	16	9.1	13	11.5	12.5	7.9	6.9	6.2	11
30	130	250	110	6.8	2.2	5.8	3.5	3.9	.25	.33	.40	.62
31	2.0	2.2	1.5	.50	.42	.43	.34	.43	.69	.80	.90	2.15
32	6.3	8.6	6.1	1.0	.48	1.35	1.1	1.2	.19	.20	.18	.24
33		.14										
39	5.6	6.7	4.3	1.6	1.1	1.6	1.25	1.6	1.25	1.0	.9	1.2
40												
41	20	22	15	4.5	3.3	5.0	4.3	5.1	2.7	2.18	2.0	2.2
42											.24	.46
43	8.4	.		2.2	1.4	2.4	1.9	2.4	1.1	.8	.8	.9
44	38	70	21	.56								
45												
46												
47												
48												
49												
50												
58	17	22	15	4.6	2.5	5.5	4.6	5.7	1.3	1.1	1.0	1.1

COMMENTS

Quenching temperature -183°C (liquid oxygen)

Reaction pressure 1 mm Hg

Helium-Oxygen flow 15.1 std. cm³/min.Ammonia flow 7 to 10 std. cm³/min.

2-methylpentane used as refrigerant during warm-up

Table 8. (Continued)

ION CURRENTS (Arbitrary Units)

Temp. °C	- 61	- 54	- 49	- 42	- 34	- 32	- 23	- 17	- 9	- 4	- 3	- 1
Press. μ	28	55	75	150	300	240	175	118	50	55	60	68
m/e												
12	6.0	6.7	9.0	22	78	22	18	16.5	10	10.5	11	11
13	1.9	2.0	2.4	3.5	17	6.0	3.2	2.8	2.3	2.4	2.6	2.8
14	52	80	88	105	310	70	100	114	62	67	78	108
15	90	115	120	100	230	105	84	77	57	68	86	86
16	330	+	450	400	960	620	540	450	270	350	390	450
17	250	+	380	410	+	+	920	530	300	450	460	520
18	16	30	90	350	+	+	+	640	420	500	450	440
24												
25					2.4							
26	1.65	1.65		2.7	11	2.8	3.1	2.7	2.7			
27	5.0	4.5	4.7	6.7	19	9.4	10	7.0	8.0	8.6	8.6	9.2
28	3.7	4.9	6.2	17	66	13	15	11.5	10.0	12.5	12	16
29	8.7	7.5	8.5	10	26	16.5	16.5	15	14	16	15	17
30	.45	.85	1.5	6.6	150	5.6	33	30	2.5	5.4	9.3	20
31	2.9	2.2	2.3	2.5	5.1	2.6	2.7	2.6	2.1	2.4	2.2	2.2
32	.27	.37	.60	1.2	10.0	2.7	3.2	1.5	.84	.96	1.0	1.0
33							.06					.10
39	1.3	1.3	1.3	1.6	5.3	4.1	3.2	2.7	2.2	2.3	2.3	2.6
40		.20	.24	.36								
41	2.2	2.5	2.8	3.9	14.5	11	8.0	6.8	5.8	6.4	6.5	6.8
42	.43	.44	.44									
43	1.0	1.1	1.2	1.7	10	4.7	3.4	2.9	2.3	2.9	3.0	2.8
44					8.8							
45												
46												
47												
48												
49												
50												
58	1.2	1.5	1.5	4.1	15	9.8	7.2	6.8	3.0	3.7	3.9	3.9

COMMENTS

Maximum evolution of nitrogen, ammonia, nitrous oxide, and diimide at -116°C

Maximum evolution of water at -34°C

Maximum evolution of hydrazine at -23°C

Evolution of hydroxylamine (m/e = 33) beginning at -1°C

Table 8. (Continued)

ION CURRENTS (Arbitrary Units)

Temp. °C	-0.5	0	+ 1	+ 2
Press. μ	70	74	60	50
m/e				
12		12.5	11.5	
13		3.1		
14	120	128	135	118
15	86	87	87	82
16	440	450	440	410
17	510	520	510	460
18	430	430	395	320
24				
25				
26				
27		9.2	9.5	9.5
28	17	17	18.5	15.5
29	17	16.5	17.8	17.5
30	22	29	30	32
31	2.3	2.2	2.25	2.45
32	1.1	1.1	1.1	1.2
33	.14	.23	.35	.65
39		2.5	2.5	2.3
40				
41		6.8	7.3	5.9
42				
43		2.8	3.2	2.7
44				
45				
46				
47				
48				
49				
50				
58		4.1	4.2	3.4

COMMENTS

Table 9. Data from $O + C_2H_2$ Reaction, -163° to $-83^\circ C$

ION CURRENTS (Arbitrary Units)

Temp. $^\circ C$	-163	-158	-155	-152	-148	-145	-142	-139	-135	-132	-129	-125
Press. μ	45	130	150		140	130	95	70	60	70	69	75
m/e												
12	6.7	16	21	19	19.5	20	17	12	9.0	9.2	10	10.5
13	12	31	39	34	33	33	27	18.5	12.8	13.5	14.8	15
14	1.3	2.2	2.6	2.4	2.2	2.3	1.9	1.3	1.0	1.1	1.2	1.2
15	1.35	.9	.85	.75	.74	.72	.62	.54	.42	.53	.53	.56
16	2.0	5.0	5.7	5.7	5.8	6.1	5.4	4.2	3.7	3.9	4.1	4.1
17	1.6	1.2	.55	.32	.28	.32	.45	.61	.84	1.1	1.5	2.0
18				1.0		1.15		2.4	3.3		5.8	8.2
24	2.4	10	19	16.5	15.0	15	10.5	6.2	4.4	5.2	5.9	6.6
25	7.3	31	58	50	45	46	31	17	12.5	14.5	17	18.5
26	.26	120	125	125				64	46	53	61	69
27	1.2	2.8	5.2	4.5	4.0	3.9	2.6	1.5	1.1	1.3	1.5	1.6
28	.9	2.2	3.5	3.3	3.1	3.2	2.4	1.7	1.5	1.7	1.8	2.0
29	1.1	.8	.9	.9	.75	.75	.61	.49	.46	.48	.48	.50
30	.1	.07	.06	.04	.04	.04	.03		.02		.03	.03
31	.20	.10	.07	.06	.06	.07	.06	.05	.05		.06	.06
32	.04	.04	.05	.06	.05	.06	.05	.04	.04	.05	.06	.06
33												
39	.16	.12	.12	.13	.14	.15	.10	.08	.08	.08	.08	.09
40												
41	.52	.44	.48	.47	.52	.53	.38	.31	.29	.29	.28	.27
42												
43												
44	.13	.78	1.6	1.75	2.0	2.15	.95	.52	.45	.55	.53	.55
45												
46												
47												
48												
49												
50												
58	.33	.37	.37	.36	.36	.35	.32	.30	.29	.28	.27	.26

COMMENTS

Quenching temperature $-183^\circ C$ (liquid oxygen)

Reaction pressure 2 mm Hg

Helium-Oxygen flow 34.2 std. $cm^3/min.$ Acetylene flow 3.0 std. $cm^3/min.$

Reaction time 30 min.

Propane used as warm-up refrigerant

Table 9. (Continued)

ION CURRENTS (Arbitrary Units)

Temp. °C	-124	-123	-119	-116	-115	-110	-109	-104	-100	- 98	- 95	- 93
Press. μ	82	88	63	33	22	20	27	24	22	20	20	
m/e												
12	10.8	12.5	8.5	3.0	3.3	3.1	3.9	3.5	3.3	2.2	2.0	2.1
13	17.5	21	13	2.9	3.1	3.1	3.7	3.6	3.7	2.2	2.0	2.1
14	1.35	1.6	1.1	.42	.44	.48	.57	.58	.65	.33	.33	.85
15	.57	.62	.53	.32	.31	.35	.46	.52	.48	.21	.23	.25
16	4.3	4.3	2.9	2.3		2.5	3.1	2.7	2.6	1.7	1.6	1.65
17	2.3	1.7	1.7	1.7		2.1	2.4	3.2	3.7	2.0	2.0	2.0
18		7.0	6.5	6.9		8.8	9.4	13	14.6	8.3	7.9	7.6
24	8.2	10.5	5.3	1.6		1.9	2.2	2.0	2.1	1.45	1.36	1.4
25	23	31	14.5	4.6		5.2	6.0	5.8	5.9	4.1	3.9	3.8
26	85	112	50	17		18.5	22	21.5	21	14.5	13.8	13.8
27	2.0	2.5	1.3	.75		.85	.96	1.05	1.15	.6	.6	.62
28	2.2	2.4	1.5	1.85		1.9	2.3	2.35	25	1.55	1.5	1.5
29	.53	.57	.49	.65		.63	.65	.71	.80	.72	.78	.83
30	.04	.05	.05	.07		.09	.10	.14	.20	.11	.14	.17
31	.06	.06	.05	.05		.05	.05	.06	.07	.06	.06	.06
32	.07	.07	.05	.08		.08	.09	.11	.13	.16	.19	.23
33												
39	.08	.09	.08	.09		.09	.10	.11	.12	.08	.09	.09
40												
41	.28	.28	.26	.30		.30	.30	.31	.31	.31	.31	.31
42												
43												
44	.62	.52	.34	.40		.43	.51	.42	.41	.32	.31	.29
45												
46												
47												
48												
49												
50												
58	.24	.23	.24	.26		.26	.26	.25	.25	.25	.25	.25

COMMENTS

Maximum evolution of unreacted C_2H_2 at $-155^\circ C$
 Maximum evolution of CO_2 at $-145^\circ C$
 Maximum evolution of secondary C_2H_2 at $-123^\circ C$
 Maximum evolution of O_2 at $-87^\circ C$
 No appearance of $HCHO$

Quenched reaction deposit red and yellow colored
 Red color fades during evolution of secondary C_2H_2
 Yellow color begins to fade during evolution of O_2

Table 9. (Continued)

ION CURRENTS (Arbitrary Units)

Temp. °C	- 90	- 87	- 83	
Press. μ	22	24	25	
m/e				
12	2.6	2.6	2.7	
13	2.3	2.9	3.1	
14	.37	.43	.46	
15	.29	.35	.55	
16	1.75	1.98	2.15	
17	1.9	1.8	1.8	
18	7.5	7.1		
24	1.6	1.8	1.84	
25	4.4	5.1	5.0	
26	16.5	18.4	18	
27	.68	.75	.83	
28	1.6	1.65	1.7	
29	.88	.90	.98	
30	.18	.19	.19	
31	.07	.09	.12	
32	.27	.29	.27	
33				
39	.10	.11	.13	
40				
41	.31	.33	.36	
42				
43				
44	.33	.34	.32	
45				
46				
47				
48				
49				
50				
58	.24	.23	.24	

COMMENTS

Table 10. Data from $O + C_2H_2$ Reaction, $-108^\circ C$ to $-20^\circ C$

ION CURRENTS (Arbitrary Units)

Temp. $^\circ C$	-108	-106	-103	- 97	- 85	- 82	- 79	- 76	- 72	- 70	- 69	- 66
Press. μ	38	31	25	22	18	18		18	18			18
m/e												
12	5.9	4.8	3.9	3.1	2.5	2.1	2.1	1.95	1.65	1.4	1.25	1.24
13	3.2	2.5	2.3	1.8	1.4	1.2	1.1	1.07	1.0	.9	.85	.88
14	.49	.49	.47	.46		.41	.43	.48	.5	.5	.5	.5
15	.73	.73	.72	.72	.82	.87	.92	1.2	1.5	1.5	1.5	1.45
16	6.1	5.0	4.1	3.5	3.0	2.7	2.5	2.4	1.9	1.75	1.65	1.56
17	3.2	3.2	3.2	3.2	3.1	3.1	3.1	3.2	3.4	3.6	3.8	4.1
18	12.5	12.2			11.9		12.0	12.1	.13	13.7	14.8	15.5
24	2.9	2.5	2.5	2.1	1.8	1.5	1.1	1.04	.84	.76	.69	.66
25	9.2	8.1	7.1	5.9	4.7	3.9	3.7	3.4	2.8	2.5	2.3	2.15
26	36	33	29	24	19.5	16	15	14	11.5	10.2	9.3	9.0
27	3.2	3.1	3.0	3.0	2.7	2.6	2.6	2.4	2.5	2.5	2.6	2.5
28	7.0	6.4	5.9	5.6	5.1	4.7	4.7	4.5	4.4	4.2	4.2	4.3
29	4.6	4.6	4.7	4.7	4.4	4.7	4.9	5.4	6.9	7.5	9.0	10.3
30	.33	.38	.46	.51	.68	.65	.62	.57	.45	.41	.36	.36
31	.88	.82	.81	.81	.76	.76	.75	.74	.76	.74	.75	.73
32	.40	.38	.39	.56	.72	.65	.63	.64	.69	.69	.66	.61
33												
39	1.18	1.05	.9	.9	.84	.80	.80	.79	.80	.78	.78	.77
40												
41	4.0	3.4	2.8	2.8	2.7	2.6	2.6	2.5	2.5	2.5	2.4	2.3
42												
43					1.6	1.45	1.45	1.45	1.5	1.42	1.38	1.28
44	7.9	4.6	3.5	2.9	2.3	1.95	1.85	1.65	1.3	1.15	1.0	.89
45					.12	.12	.13	.15	.21	.23	.30	.37
46						.06	.07	.09	.15	.18	.24	.32
47												
48												
49												
50												
58	1.9	1.5	1.05	1.0	.95	.95	.92	.9	.87	.85	.84	.84

COMMENTS

Quenching temperature $-183^\circ C$ (liquid oxygen)
 Reaction pressure 1.5 mm Hg
 Helium-oxygen flow 20 std. $cm^3/min.$
 Acetylene flow 4.9 std. $cm^3/min.$
 Reaction time 55 min.
 2-methylpentane used as warm-up refrigerant

Table 10. (Continued)

ION CURRENTS (Arbitrary Units)

Temp. °C	- 63	- 58	- 57	- 55	- 54	- 52	- 50	- 48	- 45	- 43	- 41	- 40
Press. μ		35	25	23	20	19		21	20	24	22	23
m/e												
12	1.25	1.15	1.05	.9	.7	.71	.71	.85	.87	1.0	.85	.85
13	.90	.9	.77	.61	.43	.40	.39	.43	.44	.47	.43	.41
14	.5	.5	.45	.41	.33	.33	.32	.35	.33	.35	.36	.33
15	1.3	1.55	1.3	1.1	.85	.85	.79	.91	.80	.87	1.0	.87
16	1.56	1.8	1.65	1.45	1.25	1.3	1.3	1.6	1.6	1.7	1.7	1.6
17	4.3	5.4	5.5	6.0	5.6	5.7	5.7	6.8	6.5	6.9	7.1	7.1
18	17	20.5	21.5	23	22	22	22.5	25	25	27	28	
24	.62	.49	.29	.20	.14	.13	.12	.11	.09	.07	.05	
25	2.05	1.6	.89	.59	.46	.43	.37	.40	.27	.25	.16	.15
26	8.5	6.9	3.8	2.6	1.95	1.8	1.55	1.6	1.15	1.07	.68	.65
27	2.5	2.6	2.3	2.2	2.1	2.1	2.05	2.05	2.0	2.0	2.98	1.95
28	4.6	5.7	4.7	4.3	4.0	4.1	3.9	4.3	4.5	4.5	4.6	4.3
29	12	19.5	16	14	12	12	11.7	12.8	14.7	14.5	16	14
30	.37	.50	.41	.37	.33	.33	.32	.35	.36	.37	.37	.35
31	.74	.79	.72	.71	.70	.70	.69	.70	.70	.71	.70	.67
32	.54	.67	.44	.39	.39	.38	.38	.39	.35	.32	.29	.28
33												
39	.75	.74	.79	.80	.78	.78	.77	.75	.74	.64	.63	.63
40												
41	2.25	2.3	2.1	2.0	2.1	2.1	2.1	2.02	2.0	1.98	1.95	1.94
42												
43	1.2	1.35	1.05	.98	1.0	1.0	1.0	1.0	1.0	1.0	.98	.98
44	.88	.72	.65	.51	.55	.61	.58	.71	.72	.75	.71	.69
45	.43	.68	.64	.56	.51	.49	.47	.53	.57	.65	.58	.60
46	.37	.60	.56	.50	.45	.43	.41	.44	.51	.57	.52	.56
47												
48												
49												
50												
58	.82	.80	.78	.73	.79	.79	.77	.77	.77	.75	.74	.74

COMMENTS

Maximum evolution of O_2 at $-85^\circ C$ Appearance of $HCOOH$ at $-82^\circ C$ Appearance of H_2O at $-76^\circ C$ Maximum evolution of $(CHO)_2$ at $-58^\circ C$

White solid remains in reactor at room temperature

Table 10. (Continued)

ION CURRENTS (Arbitrary Units)

Temp. °C	- 35	- 34	- 31	- 30	- 29	- 28	- 27	- 25	- 23	- 22	- 20	
Press. μ	24	24	28	24	25	28	28	29	28	18	15	
m/e												
12	.83	.83	.9			.89	.89	.90	1.0	.68	.41	
13	.43	.48	.5				.57	.60	.68	.43	.25	
14	.32	.32	.33			.36	.36	.37	.40	.33	.27	
15	.81	.77	.81	.86	.85	.95	.95	.95	1.1	.85	.67	
16	1.58	1.5	1.7	1.5	1.5	1.55	1.58	1.55	1.65	1.2	.95	
17	9.2	7.5	7.7				7.1	7.3	7.4	6.2	5.6	
18	27	29	30				28	28	29	24	22	
24												
25	.13	.11	.11				.09				.14	
26	.55	.47	.46			.40	.41	.39	.39	.55	.62	
27	1.95	1.9	1.95			1.95	1.95	1.95	1.95	1.95	1.95	
28	4.3	4.5	5.0	4.4	4.9	5.1	5.0	5.0	5.3	3.4	3.2	
29	14.2	16.5	19.5	16	19.5	20.4	20.1	19.5	21.5	10.8	9.1	
30	.36	.38	.43	.39		.45	.45	.44	.48	.29	.27	
31	.67	.67	.69			.70	.70	.71	.74	.65	.66	
32	.28		.25			.25	.25	.26	.25	.26	.27	
33												
39	.62	.61	.60			.61	.61	.62	.63	.64	.67	
40												
41	1.9	1.88	1.85			1.85	1.85	1.85	1.9	2.0	2.1	
42												
43	.97	.9	.95	.95	.95	.95	.95	.95	11.0	.89	.92	
44	.64	.59	.69	.59	.63	.65	.61	.63	.63	.34	.35	
45	.55	.65	.86	.69	.95	.90	.95	.90	.44	.39	.39	
46	.53	.61	.81	.58	.77	.83	.84	.90	.85	.35	.34	
47												
48												
49												
50												
58		.72	.72		.73	.72	.72	.73	.73	.75	.80	

COMMENTS

Table 11. Data from $O + C_2H_4$ Reaction, -173° to $-104^\circ C$

ION CURRENTS (Arbitrary Units)

Temp. $^\circ C$	-173	-163	-160	-157	-154	-152	-149	-145	-140	-137	-133	-131
Press. μ		15	15	15	15	15	10	10	12	12	12	18
m/e												
12		.95	1.2	1.2	.74	.69	.70	1.1	1.2	1.2	1.0	1.1
13		.56	.49	.45	.45	.37	.22	.26	.45	.62	.90	1.15
14		1.2	1.1	1.0	.98	.92	.55	.74	1.0	1.25	1.4	1.55
15		.30	.29	.28	.27	.26	.22	.23	.22	.23	.23	.25
16		1.1	1.6	1.35	.85	.80	.92	1.45	1.6	1.4	.93	.85
17		.5	.5	.5	.54	.62	.72	.9	1.1	1.4	1.8	2.1
18		2.1	1.9	1.9	2.0	2.15	2.3	3.0	3.7	4.6	5.4	7.0
24	.42	.32	.22	.24	.23		.07	.07	.06	.03		
25	1.3	1.1	.78	.71	.73		.24	.22	.18	1.3	.06	
26	5.8	4.6	3.3	3.2	3.2		1.1	.93	.77	.56	.25	.19
27	5.2	4.5	3.2	3.2	3.1		1.2	1.1	.90	.62	.47	.43
28	8.5	6.7	5.3	5.4	5.2		2.6	2.4	2.6	2.6	2.8	3.2
29	.95	1.0	.9	.92	.9		.92	1.3	2.5	3.4	5.6	7.6
30	.10	.08	.08	.06	.06		.10	.51	1.2	2.0	3.4	4.4
31	.08	.08	.08	.08	.06		.06	.07	.06	.06	.10	.11
32	.10	.12	.12	.13	.14		.20	.24	.30	.36	.31	.25
33												
39	.07	.11		.12	.13	.13	.13	.12	.12	.11	.11	.10
40												
41	.44	.51	.53	.55	.56	.56	.57	.53	.53	.52	.51	.50
42		.05	.05	.07	.08	.08	.08	.07	.09	.09	.09	.07
43	.16	.20	.20	.21	.22	.22	.23	.21	.21	.20	.20	.19
44		.26	.47	.59	.30	.28	.36	.43	.42	.32	.13	.06
45												
46												
47												
48												
49												
50												
58	.36	.44	.42	.49	.51	.52	.46	.53	.52	.51	.51	.50

COMMENTS

Quenching temperature $-177^\circ C$ (propane refrigerant)

Reaction pressure 1 mm Hg

Helium-oxygen flow 15.1 std. $cm^3/min.$ Ethylene flow 3 std. $cm^3/min.$

Reaction time 60 min.

Table 11. (Continued)

ION CURRENTS (Arbitrary Units)

Temp. °C	-129	-127	-125	-123	-121	-119	-117	-115	-113	-111	-105	-104
Press. μ	20	22	22	22	22	22	28	34	42	48	44	30
m/e												
12	1.25	1.35	1.4	1.25	1.0	.95	1.1	1.2	1.45	1.7	1.7	1.3
13	1.35	1.55	1.6	1.45	1.4	1.55	2.1	2.5	3.2	3.8	3.7	2.9
14	1.6	1.8	1.9	2.1	3.0	4.5	7.0	9.3	10.5	13.5	13	10
15	.3	.48	.85	2.35	6.1	11.5	19.5	27	33	39	37	28
16	.9	.95	1.0	1.2	1.6	2.7	4.0	5.2	6.6	8	9.4	5.6
17	2.6	3.2	3.9	5.3	8.3	11	16	20	27	36	50	22
18	7.4	10	12	17	26	34	51	67	89	125	135	72
24					.05	.08	.14	.19	.22	.25	.24	.18
25				.09	.20	.32	.54	.70	.88	1.0	.98	.70
26	.16	.14	.15	.25	.45	.71	1.1	1.35	1.65	1.85	1.85	1.35
27	.41	.37	.40	.48	.59	.73	.95	1.05	1.25	1.35	1.45	1.20
28	3.4	3.8	3.7	3.1	2.4	2.0	1.65	1.6	1.55	1.65	1.85	1.4
29	8.4	9.7	9.6	8.1	7.5	8.0	10	11.5	13.5	14.8	14.8	10
30	5.3	5.8	5.7	4.3	2.8	1.7	1.0	.65	.53	.47	.43	.3
31	.12	.13	.13	.12	.10	.10	.11	.12	.12	.13	.11	.09
32	.24	.17	.14	.12	.12	.11	.12	.11	.10	.11	.13	.15
33												
39	.08	.11	.11	.10	.11	.12	.12	.12	.13	.14	.15	.16
40												
41	.49	.47	.49	.45	.48	.49	.49	.50	.50	.50	.49	.45
42	.07	.07				.12	.17	.20	.24	.26	.25	.21
43	.18	.19	.19	.20	.21	.27	.36	.41	.47	.51	.50	.40
44		.05			.14	.28	.49	.65	.79	.89	.85	.67
45												
46												
47												
48												
49												
50												
58	.48	.47	.47	.46	.46	.44	.44	.42	.40	.37	.37	.35

COMMENTS

Quenched Reaction Deposit yellow colored

Unreacted ethylene being pumped away -173° to -137°C

Evolution of CO_2 -163° to -131°C

Maximum evolution of CH_3CHO - CH_3OCH_2 mixture at -111°C

Maximum evolution of HCHO at -127°C

Table 12. Data from $O + C_2H_4$ Reaction, -124° to $-10^\circ C$

ION CURRENTS (Arbitrary Units)

Temp. $^\circ C$	-124	-121	-116	-115	-110	-106	-103	-101	-97	-94	-85	-82
Press. μ	20	16	15	15	15	15	14	12	10	11	10	11
m/e												
12	2.3	1.15	.77	.59	.61	.62	.42	.34	.26	.26	.24	.32
13	1.1	.6	.51	.70	1.0	1.1	.7	.51	.37	.36	.32	.47
14	1.2	.85	1.25	2.3	3.3	3.7	2.6	1.95	1.6	1.45	1.4	2.05
15	.43	.89	2.6	6.0	9.1	10.5	6.5	4.7	4.0	3.5	3.3	5.2
16	2.1	1.3	1.3	1.5	1.65	1.7	1.2	.99	1.0	.97	.94	1.3
17	1.6	1.6	1.8	2.7	2.3	2.0	1.8	1.7	1.7	1.75	1.85	1.9
18	5.8	6.5	6.7	9.5	7.8	6.6	5.1	5.6	5.5	5.7	6.2	6.2
24				.05	.07	.07	.05	.03				.04
25	.04	.07	.11	.20	.25	.27	.24	.12	.12	.12	.11	.15
26	.20	.32	.42	.54	.59	.59	.51	.36	.34	.35	.33	.40
27	.72	.65	.66	.72	.70	.66	.60	.53	.54	.55	.60	.68
28	3.6	2.5	2.0	1.4	1.15	.98	.92	.85	.85	.88	.94	1.0
29	7.1	4.8	4.1	4.0	4.5	4.2	3.5	2.0	1.9	1.9	2.05	2.9
30	4.3	2.4	1.4	.46	.25	.18	.15	.15	.20	.27	.51	.74
31	.19	.10	.07	.08	.06	.05	.05	.04	.04	.05	.08	.13
32	.19	.25	.31	.18	.13	.12	.13	.16	.19	.23	.19	.20
33												
39	.12	.13	.14	.15	.13	.12	.11	.10	.11	.11	.12	.14
40		.02	.02	.02	.02							
41	.43	.56	.67	.69	.62	.55	.53	.50	.50	.48	.49	.53
42	.05	.08	.11	.14	.14	.12	.11	.07	.07	.07	.08	.10
43	.18	.24	.30	.36	.36	.32	.28	.23	.21	.21	.21	.23
44	.28	.27	.30	.37	.39	.34	.23	.12	.10	.10	.11	.16
45												
46												
47												
48												
49												
50												
58	.83	.14	.24	.40	.56	.70	.70	.63	.60	.58	.55	.54

COMMENTS

Quenching temperature $-183^\circ C$ (liquid oxygen)

Reaction pressure 1.3 mm Hg

Helium-oxygen flow 24.0 std. cm^3/min .Ethylene flow varied 0.85 to 3.01 std. cm^3/min .

Reaction time 75 min.

2-methylpentane used as warm-up refrigerant

Table 12. (Continued)

ION CURRENTS (Arbitrary Units)

Temp. °C	- 80	- 76	- 74	- 71	- 68	- 65	- 60	- 58	- 54	- 50	- 46	- 42
Press. μ	15	16	16	18	19	19	18	19	21	30	35	35
m/e												
12	.39	.38	.43	.50	.55	.48	.42	.43	.51	.51	.45	.42
13	.59	.61	.68	.81	.86	.72	.63	.63	.69	.67	.62	.59
14	2.5	2.4	2.7	3.3	3.2	2.7	2.2	2.1	2.0	1.95	1.6	1.45
15	6.5	6.6	7.3	9.4	9.4	7.5	6.5	6.0	6.0	5.4	4.5	4.1
16	1.4	1.5	1.55	1.8	1.7	1.4	1.2	1.3	1.4	1.5	1.5	1.5
17	2.0	2.0	2.0	2.0	2.0	2.2	2.4	3.0	4.1	5.3	7.2	8.8
18	6.2	6.6	6.7	6.7	6.9	7.4	8.2	10.5	13.5	25	30	
24	.04		.04		.06							
25	.17	.18	.19	.22	.23	.19	.16	.18	.18	.16	.12	.12
26	.45	.42	.45	.51	.54	.51	.48	.49	.5	.42	.30	.30
27	.76	.92	1.08	1.3	1.65	1.9	2.3	2.5	2.1	1.7	1.3	1.1
28	1.0	1.0	1.05	1.1	1.15	1.15	1.3	1.3	1.3	1.15	1.1	1.05
29	3.4	3.5	4.0	4.6	4.8	4.7	4.7	4.9	4.2	3.8	3.2	3.0
30	.86	.86	.86	.84	.50	.37	.32	.32	.26	.23	.19	.19
31	.17	.28	.38	.52	.80	.97	1.5	1.75	1.25	1.0	.7	.56
32	.18	.17	.18	.19	.16	.12	.10	.09	.08	.08	.08	.08
33												
39	.15	.20	.25	.30	.40	.51	.63	.67	.54	.43	.34	.30
40				.08	.10	.12	.12	.10	.08	.06		
41	.57	.68	.75	.83	1.0	1.3	1.5	1.6	1.3	1.1	.91	.75
42	.10	.12	.14	.16	.18	.21	.23	.25	.20	.18	.16	.14
43	.25	.29	.34	.39	.44	.49	.55	.59	.52	.48	.44	.40
44	.19	.19	.22	.25	.22	.19	.17	.17	.16	.15	.12	.11
45							.05	.06	.07	.09	.10	.10
46								.04	.04	.03	.03	.03
47												
48												
49												
50												
58	.48	.47	.50	.51	.54	.57	.63	.64	.54	.51	.48	.46

COMMENTS

Maximum evolution of water at -40°C Appearance of formic acid at -60°C Maximum evolution of methanol at -68°C Maximum evolution of $\text{CH}_3\text{CHO} - \text{CH}_2\text{OCH}_2$ mixture at -110°C

Table 12. (Continued)

ION CURRENTS (Arbitrary Units)

Temp. °C	- 38	- 35	- 30	- 26	- 22	- 15	- 14	- 10	
Press. μ	35	30	25	25	25	25	25	25	
m/e									
12	.39	.37	.39	.39	.43	.43	.42	.41	
13	.55	.56	.54	.54	.62	.60	.54	.50	
14	1.35	1.25	1.35	1.35	1.5	1.45	1.3	1.25	
15	3.6	3.3	3.5	3.4	3.8	3.5	3.0	2.7	
16	1.4	1.3	1.2	1.2	1.2	1.1	1.2	1.2	
17	8.8	7.6	6.7	6.0	6.1	6.0	5.8	5.7	
18		27	23.5		21	21	30		
24									
25	.11	.10	.11	.10	.11	.10	.09	.09	
26	.30	.32	.32	.32	.32	.32	.32	.32	
27	1.1	1.1	1.1	1.15	1.2	1.25	1.3	1.35	
28	1.1	1.2	1.2	1.25	1.3	1.35	1.4	1.4	
29	2.9	2.7	2.9	3.2	3.4	3.5	3.5	3.5	
30	.22	.27	.36	.52	.73	.95	1.2	1.4	
31	.54	.52	.53	.55	.58	.60	.64	.66	
32	.08	.08	.07	.08	.09	.09	.10	.10	
33									
39	.30	.28	.28	.29	.30	.32	.33	.35	
40				.06					
41	.80	.78	.79	.82	.84	.87	.93	.95	
42	.14	.13	.13	.14	.15	.15	.16	.16	
43	.41	.38	.40	.43	.46	.47	.47	.47	
44	.09		.08	.09	.09	.09	.09	.09	
45	.10	.10	.10	.12	.12	.12	.10	.05	
46	.03	.03	.03	.04	.05	.05	.05	.05	
47									
48									
49									
50									
58	.47	.43	.44	.46	.46	.47	.48	.49	

COMMENTS

Quenched reaction deposit yellow colored
Clear, yellow tinted liquid present at -110°C
Liquid pumped away at -102°C , leaving a white solid in reactor
Presence of an accompanying clear film noted at -80°C

Table 13. Data from $O + C_2H_6$ Reaction, -177° to $-95^\circ C$

ION CURRENTS (Arbitrary Units)

Temp. $^\circ C$	-177	-174	-170	-166	-162	-158	-154	-150	-146	-142	-138	-133
Press. μ		2										
m/e												
12	.20	.16	.14	.12	.12	.09	.09	.08	.08	.08	.09	.09
13	.06	.04	.04	.03	.04							
14	.30	.30	.35	.29	.25	.25	.23	.23	.23	.23	.24	.24
15	.40	.32	.34	.29	.24	.22	.22	.21	.21	.22	.22	
16	.40	.32	.30	.27	.22	.23	.23	.22	.23	.24	.27	.32
17	.55	.29	.24	.22	.22	.25	.25	.3	.36	.55	.82	
18	2.0	1.05	.82	.76	.83	.92	.97	1.2	1.5	2.3	3.5	
24												
25	.06											
26	.26	.21	.20	.22	.13	.13	.13	.16	.18	.20	.23	.26
27	.95	.60	.52	.52	.42	.43	.44	.46	.48	.51	.52	.58
28	1.65	1.5	1.25	1.25	1.0	1.05	1.1	1.2	1.25	1.35	1.45	1.5
29	1.65	1.0	.8	.84	.8	.8	.8	.8	.8	.8	.81	.81
30	.21	.13	.11	.11	.07	.07	.07	.08	.09	.11	.11	.12
31	.16	.08	.06	.06	.05	.05	.05	.05	.05	.06	.05	.04
32	.20	.16	.12	.12	.13	.13	.14	.14	.16	.17	.18	.18
33												
39	.18	.13	.09	.10	.10	.10	.10	.10	.10	.10	.10	
40												
41	.80	.62	.52	.48	.49	.49	.48	.48	.47	.47	.46	.44
42	.11	.08	.06									
43	.34	.24	.19	.18	.18	.18	.18	.18	.16	.18	.18	.18
44												
45												
46												
47												
48												
49												
50	.03											
58	.67	.64	.59	.58	.55	.55	.54	.52	.50	.49	.46	

COMMENTS

Quenching temperature -169° to $-176^\circ C$ (liquid propane)

Reaction pressure 1.4 to 1.8 mm Hg

Helium-oxygen flow varied 18 to 28 std. cm^3/min .Ethane flow varied 1.0 to 8.5 std. cm^3/min .

No appearance of formaldehyde, carbon dioxide, ozone, or acetaldehyde

Only contaminating nitrogen dioxide observed in temperature range of warm-up

Table 13. (Continued)

ION CURRENTS (Arbitrary Units)

Temp. °C	-123	-120	-114	-110	-108	-103	-100	- 97	- 95	
Press. μ	5	5	5			9	10	12	17	
m/e										
12	.13	.16	.16	.15	.16	.20	2.5	.34	.29	
13					.12	.15	.18	.28	.23	
14	.27	.33	.46	.60	.70	.96	1.3	1.95	2.4	
15	.31	.37	.65	.69	.73	.88	1.15	1.95	2.6	
16	.59	.82	1.05	.75	.88	1.35	2.0	3.2	4.3	
17	3.9	6.1	9.2	4.4	4.3	4.5	4.7	5.2	5.2	
18	16	25	36	18	17.5	18.5	20	20.5	20.5	
24										
25			.09	.12	.17	.20	.26	.33	.10	
26	.28	.31	.39	.54	.73	.90	1.1	1.35	.28	
27	.61	.65	.69	.76	.80	.9	1.0	1.2	.80	
28	1.7	1.75	1.75	1.85	2.1	2.4	2.8	3.3	2.6	
29	.85	.92	1.02	1.1	1.15	1.3	1.6	2.3	2.7	
30	.19	.32	.68	1.2	1.85	3.5	5.4	9.0	12.5	
31	.05	.05	.06	.06	.07	.08	.10	.13	.15	
32	.21	.20	.18	.19	.20	.24	.25	.30	.30	
33										
39	.11	.11	.11	.10	.11	.13	.13	.15	.15	
40										
41	.42	.41	.39	.37	.38	.41	.43	.46	.50	
42								.09	.10	
43	.17	.16	.15	.16	.16	.17	.18	.20	.23	
44				.05	.05	.08	.10	.14	.15	
45										
46						.07	.14	.23	.36	
47										
48										
49										
50										
58	.40	.32	.35	.34	.33	.32	.33	.33	.32	

COMMENTS

Table 14. Data from $O + C_2H_6$ Reaction, -111° to $-37^\circ C$

ION CURRENTS (Arbitrary Units)

Temp. $^\circ C$	-111	-108	-104	-100	- 97	- 94	- 91	- 87	- 82	- 79	- 74	- 72
Press. μ				11		12	12		11			12
m/e												
12	.54	.50	.49	.44	.42	.45	.49	.50	.70	.76	.56	.36
13	.12	.12	.13	.15	.18	.20	.24	.28	.47	.50	.38	.23
14	.58	.66	.76	.90	.95	1.05	1.1	1.2	1.65	1.6	1.1	.95
15	1.25	1.25	1.4	1.65	1.98	1.98	2.15	2.35	3.3	3.2	2.5	2.6
16	1.35	1.55	1.65	1.85	1.85	1.85	1.92	2.05	2.2	1.9	1.4	1.2
17	1.35	1.45	1.55	1.65	1.65	1.65	1.65	1.72	1.7	1.7		2.1
18	4.7	5.1	5.1	5.2	5.3	5.3		5.6	4.5	4.6		7.9
24							.04	.04				
25	.07	.06	.07	.08	.09	.12	.15	.17	.13	.13		.09
26	.33	.30	.31	.36	.41	.49	.58	.68	.53	.54		.39
27	1.3	1.25	1.25	1.25	1.3	1.32	1.35	1.0	.95	.95	.97	.97
28	1.55	1.50	1.45	1.45	1.45	1.45	1.55	1.6	1.05	1.05	1.45	1.45
29	2.0	1.95	1.95	1.95	1.95	2.0	2.05	2.15	1.55	1.5	2.2	2.25
30	.82	1.2	1.5	1.9	1.9	1.9	1.95	2.05	.95	.80	.9	.78
31	.46	.48	.49	.49	.49	.48	.50	.48	.68	.64	.45	.44
32	.32	.35	.29	.27	.27	.29	.31	.32	.10	.11	.25	.27
33												
39												
40												
41												
42												
43	.44	.41	.41	.41	.41	.40	.38	.32	.29	.30	.37	.37
44	.14	.14	.13	.11	.12	.10		.06				
45	.02	.02	.02	.02	.02						.02	
46	.02		.05	.06	.06	.07	.07	.05	.03	.03	.04	.04
47												
48												
49												
50												
58	.92	.90	.87	.85	.83	.81	.79	.63	.55	.54	.67	.66

COMMENTS

Quenching temperature $-183^\circ C$ (liquid oxygen)

Reaction pressure 1.6 mm Hg

Helium-oxygen flow 23 std. $cm^3/min.$ Ethane flow varied 1.0 to 8.5 std. $cm^3/min.$

2-methylpentane used as warm-up refrigerant

Table 14. (Continued)

ION CURRENTS (Arbitrary Units)

Temp. °C	-70	-66	-64	-60	-58	-55	-53	-51	-46	-44	-40	-37
Press. μ		13				15			22			
m/e												
12	.34	.32	.23	.20	.18	.22	.24	.47	.43	.33	.33	.29
13	.24	.24	.21	.18	.17	.19	.21	.43	.42	.42	.38	.28
14	.88	.86	.76	.64	.61		.68	1.15	1.25	1.15	1.0	.7
15	2.6	2.5	2.0	1.7	1.65	1.70	1.85	2.9	3.2	3.0	2.5	1.6
16	1.1	1.0	.72	.68	.76	.82	.98	1.6	1.5	1.5	1.4	1.2
17	2.4	2.9	3.5	4.1	4.5			7.2			10	9.5
18	9.1	11.2		15.5								
24												
25	.10	.11	.09	.06	.05	.05	.05	.16	.09	.09	.05	
26	.41	.45	.41	.26	.21	.19	.23	.5	.3	.27	.20	.16
27	1.45	1.45	1.4	1.2	1.1	1.15	1.30	1.75	1.5	1.3	1.25	1.2
28	1.5	1.6	1.5	1.15	1.01	1.0	1.05	1.5	1.15	1.08	1.1	1.1
29	2.3	2.2	2.1	2.0	2.05	2.0	2.35	3.1	3.1	3.0	3.0	2.5
30	.59	.44	.34	.29	.31	.38	.48	.58	.56	.53	.58	.55
31	.42	.40	.39	.39	.42	.49	.62	1.0	.76	.63	.58	.50
32	.26	.23	.15	.12	.14	.16	.21	.22	.20	.16	.16	.12
33												
39												
40												
41												
42												
43	.37	.37	.36	.36	.37	.39	.44	.52	.42	.42	.40	.38
44			.06			.07	.07					
45	.02	.02		.03	.03	.03	.04	.05	.05	.05	.05	.04
46	.03	.03	.02		.03	.03	.04	.04	.04	.04	.04	.03
47												
48												
49												
50												
58	.66	.65	.63	.64	.65	.69	.73	.84			.69	.67

COMMENTS

Ozone condensed in reactor at 90°K

Maximum evolution of nitrogen dioxide at -87°C

Maximum evolution of ethanol at -51°C

Table 15. Data from $O + C_2H_6$ Reaction, -163° to $-57^\circ C$

ION CURRENTS (Arbitrary Units)

Temp. $^\circ C$	-163	-154	-149	-140	-136	-131	-124	-122	-120	-118	-116	-112
Press. μ												
m/e												
12		2			5				2			
13		3			7				2			
14								43	35			106
15	13	12	13	12	11	8	6	2	2	2.5	2.5	4
16		49		48				18	20			76
17	14.5	12	13	10	17	16	13	9	10	18	15	22
18	46	52		48	53		33	30	24			80
24					8							
25	11	11	9	18	19	18			5			
26	49	51	40	56			35		13	6	2	4
27							17		11	9	10	8
28												
29	50	51	39	35	40	36	17		27	10	10	11
30		48	41	36	40	32	20	27	24	21	50	63
31												
32												
33												
39	6	20	17	32	37	32	13					
40	13	21	22	34	39	39	14		7	7	9	9
41	8	13	8	8	8	8				3	4	6
42	4	8	7	6	5							
43	6	7	6	4	5					7	6	10
44	7	8	8	13	15	8	8		6	3		3
45												
46							1		.4	6	11	26
47												
48												
49												
50												
58												

COMMENTS

Comparison experiment using TOF cryogenic inlet system
 Quenching temperature $-183^\circ C$
 Reaction pressure unknown
 Helium-oxygen flow 18 std. $cm^3/min.$
 Ethane flow 8.5 std. $cm^3/min.$

Table 15. (Continued)

ION CURRENTS (Arbitrary Units)

Temp. °C	-108	-103	-100	- 96	- 94	- 88	- 83	- 79	- 73	- 67	- 62	- 57
Press. μ												
m/e												
12						3	3	7				
13						10	14	26		16		
14		116	124	115	120	160	180	200	300	152	90	85
15	5	21	32	40	30	80	200	360	920	1140	75	38
16	64	108	112	180	190	240	240	240	120	60	50	50
17	22	44	50	80	30	40	40	38	60	72	110	175
18	86	140	184	280	100	120	100	120	160	280	420	550
24								2				
25						4	6	11				
26	6	6	12			20	34	50	120	36		9
27	6	14	16			34	42		160	56	38	34
28				500	500	540	560	600	880	480		450
29	14	21	30	50	60	240	520	840	2160	280	160	80
30	83	192	200	500	800	1160	1400	1440	720	120	70	38
31				12	20	40	140	200	500	128	35	22
32		174	176	165	150	160	144	140	200	144	130	120
33												
39						12	13				16	20
40	9	9				12	10	23			9	8
41						10	14			24	35	36
42						20	30		120	34	17	8
43	14	48	61	85	90	200	380	600	1440	240	140	85
44		7		18	20	70	100	160	280	364	222	16
45				5		32	56	120	240	60	15	14
46	43	112	200	510	620	800	1000	920	120	24	8	6
47												
48												
49												
50												
58	3	6	12	20	20	60	100	200	400	88	28	22

COMMENTS

Ozone spectra observed at 90°K

Ozone mass assignment confirmed by rough appearance potential measurement using vanishing current method

Maximum nitrogen dioxide evolution at -79°K

Nitrogen dioxide mass assignment also confirmed by rough appearance potential measurement

Ethanol observed at -73°K

Ethanol mass assignment confirmed by cracking pattern spectra

APPENDIX C

LOW TEMPERATURE REACTION OF OZONE AND AMMONIA

During the initial work on the atomic oxygen-ammonia reaction, the products were condensed to 90° or 77°K . The 90°K quenching produced a yellow colored deposit of reaction products which were described in Chapter III. In contrast, the 77°K quenching produced an orange-red reaction product deposit.

Further work on the 77°K quenching process showed that the orange-red deposit was produced by the reaction of ozone with ammonia rather than by the reaction of oxygen atoms with ammonia. This was demonstrated by condensing a layer of ammonia on top of a layer of ozone which had been previously condensed to 77°K . A bright yellow colored deposit was produced at 77°K , and as the reactor was slowly warmed, the yellow color began to change to the orange-red color. In another experiment, it was found that the orange-red solid could be formed at 90°K if the oxygen atoms produced by the electrical discharge were forced to strike the liquid oxygen cooled reactor wall before contacting a gaseous stream of ammonia. Ozone was presumably formed at the cold reactor wall by the reaction



The gaseous ozone then contacted the ammonia and the orange-red deposit was again formed.

During a controlled warm-up with continuous pumping, it was observed that the orange-red solid disappeared at -70°C and at room temperature, a white deposit remained in the reactor. Qualitative chemical analysis identified the white solid as ammonium nitrate.

The gases evolved from the reactor during the warm-up process were identified by use of both mass spectrometric cryogenic inlet systems. The resulting identifications are shown in Table 16. Since the vapor

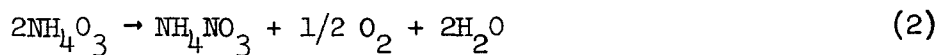
Table 16. Identified Products from $\text{O}_3 + \text{NH}_3$ Reaction

Temperature, $^{\circ}\text{C}$	Product
-153	appearance of ozone
-136	maximum evolution of ozone
-126	disappearance of ozone
-112	maximum evolution of oxygen
0	water condensed in reactor
room temperature	ammonium nitrate

pressure of ozone is 1 mm Hg at -180.4°C , any unreacted ozone present in the reactor would have been seen at temperatures lower than -153°C . Therefore, the ozone and oxygen that appeared at this temperature were apparently products of decomposition. The presence of the oxygen, water, and ammonium nitrate, and also the initial orange-red color, suggested that the colored reaction product might be NH_4O_3 , ammonium ozonide.

Solomon and coworkers (97) carried out a low temperature ozonization of ammonia and reported the formation of an orange-red solid which was only stable below -126°C . The product decomposed to yield ammonium nitrate, oxygen, and water with a total N/H/O ratio of 1/4.38/3.0.

Electron paramagnetic resonance studies indicated the presence of an unpaired electron which was typical of the ozonide ion. The visible absorption spectrum was obtained and compared with that of other known ozonide compounds. All spectra showed absorption in the region of 450 mμ which is also characteristic of the ozonide ion. From these studies, Solomon and coworkers identified the red-orange solid as NH_4O_3 , and suggested that it would decompose according to



Herman and Giguère (98) also carried out the low temperature ozonization of ammonia and reported the formation of the orange-red solid. They studied the infrared spectra of the solid as a function of temperature and assigned bands at 800, 1140, 1260, and 2053 cm^{-1} to the O_3^- ion. The maximum concentration of the ozonide ion was reported to occur upon warming to -115°C .

The results obtained from the present work are in agreement with these literature descriptions and indicate that NH_4O_3 has been produced. Since NH_4O_3 can be classified as a low temperature chemical (stable only below room temperature), it is a prime candidate for study using the TOF mass spectrometer and cryogenic inlet system with which accurate energy measurements may be made. The results presented in Table 16 were taken from two somewhat hurried initial experiments and need to be confirmed.

APPENDIX D

ENERGY EXCHANGE BETWEEN EXCITED ARGON AND NITRIC OXIDE

During the work on the atomic hydrogen-nitric oxide reaction, argon was often used as a diluent in the hydrogen gas feed stream. The presence of any reactive impurities (particularly oxygen) in the argon was explored by combining argon with nitric oxide and condensing the resulting mixture to 77°K. Only white nitric oxide was condensed and, as discussed in Chapter II, this was a sufficient test for the absence of oxygen.

However, when argon was subjected to the electric discharge and then mixed with the nitric oxide, the dark gas was again caused to emit a glow which filled the U-tube reactor and a mixture of red and black compounds was condensed at 77°K. On warming, the red and black colors began to disappear with the simultaneous appearance of a blue liquid. Room temperature mass spectrometric analysis of the gases evolved from the reactor confirmed the presence of nitric oxide and nitrogen dioxide.

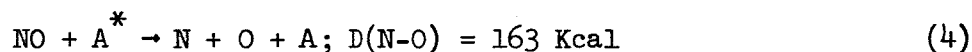
The blue liquid and the black solid were both probably dinitrogen trioxide. N_2O_3 exists as a black solid melting at $-102^{\circ}C$ to form a blue liquid (78, 99). N_2O_3 has not been observed in the gas phase and it is believed (99) that it dissociates at room temperature according to



The detection of NO and NO_2 in this thesis research supports the proposal of Equation (3).

The red material was not identified, however, recent work by Parts and Miller (100) suggested that it might be nitrosonium nitrate, NO^+NO_3^- . Parts and Miller conducted a low temperature ($77^\circ\text{--}90^\circ\text{K}$) oxidation of nitric oxide in ethane-propane solution by bubbling molecular oxygen through the solution. A red compound was formed which was stable up to 205°K . Low temperature infrared studies of the compound resulted in its characterization as nitrosonium nitrate.

The apparent presence of the nitrogen oxides NO , NO_2 , N_2O_3 , and N_2O_4 , suggested that the excited argon transferred a sufficient amount of energy to the nitric oxide to cause partial dissociation into nitrogen and oxygen atoms. The atoms then combined in various ways to form the colored products. The several reactions could possibly be represented as:



Since N_2O_3 and NO^+NO_3^- have not been observed as such in the gas phase at room temperature, the compounds would be likely candidates for study with the TOF spectrometer and cryogenic inlet system.

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Abbreviations in this Bibliography follow the form used by Chemical Abstracts (1965).

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VITA

Donald Bernard Bivens was born in Cleveland, Tennessee on May 30, 1939. He attended public schools in Cleveland, Tennessee, graduating from Bradley Central High School in June, 1957. He entered the University of Tennessee in September, 1957 and was awarded the degree of Bachelor of Science in Chemical Engineering, Magna Cum Laude, Cooperative Plan, in June, 1962. His employer under the cooperative plan was Southern Chemical Cotton Company, Chattanooga, Tennessee. While at the University of Tennessee, he held a University Freshman Scholarship and a Dixie Foundation Scholarship.

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